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Decomposition of Spinacene Hexahydrochloride by Heat.

I have previously directed attention to the fact that, when this compound is heated to a temperature above its melting point, hydrogen chloride is liberated. 2·14 Grams of the hydrochloride were introduced into a weighed test-tube, which was connected with a vacuum pump. The tube was then immersed in an oil-bath and heated for four hours to 150°. Hydrogen chloride was freely evolved, particularly at the commencement of the experiment, and at the end of the above time it was found that 0·32 gram of hydrogen chloride had been lost. The heating was then continued, but as the evolution of gas became very slow, the temperature of the bath was raised to 190°, at which temperature it was maintained for seven hours. At the end of this time, a further 0·36 gram of hydrogen chloride had been given off, making a total loss of 0·68 gram, the total amount present in the hydrochloride taken being 0·76 gram. At this point, the evolution of hydrogen chloride had become so slow that the experiment was stopped.

The oil remaining in the tube was fairly mobile and of a pale red colour. The iodine value of this oil was 255·5, and it contained Cl = 5·2 per cent. A 10 per cent. solution in benzene was found to be optically inactive.

From this experiment, it would appear that the hydrocarbon left after expelling the hydrogen chloride by heat differs from the original spinacene in being less unsaturated, due probably to the occurrence of some intramolecular change, such as that involved in the conversion of pinene into camphene. The molecular weight of this oil determined by the depression of the freezing point in benzene solution was 479, showing that, in addition to the above intramolecular change, there had been some polymerisation.

Action of Hydrogen Bromide. Spinacene Hexahydrobromide.

Dry hydrogen bromide was passed into a well-cooled solution of spinacene in several times its volume of dry ether. Shortly after the liquid had become saturated, a white substance formed, which appeared to consist of a crystalline substance and an oil. A further quantity of dry ether was added, and the precipitate was separated, washed with ether, and dried. This substance was purified by dissolving it in benzene, adding alcohol until the separation of the compound just commenced, and finally by recrystallisation from benzene alone. After three recrystallisations, the product appeared to be pure, and gave on analysis the following results:

394958

0·2061 gave 0·2640 AgBr. Br = 54·51.

$C_{29}H_{48}$,6HBr requires Br = 54·42 per cent.

As in the case of the hydrochloride, it will be seen that this percentage accords much better with the formula $C_{29}H_{48}$ than with $C_{30}H_{50}$, the theoretical percentage of bromine in the latter case being 53·57.

The hexahydrobromide is a brilliant, white, crystalline compound closely resembling the hydrochloride in appearance as well as in respect of its solubility in the commoner solvents. As in the case of the hexahydrochloride, the yield is not very large, oily compounds being formed at the same time. Thus, in one experiment in which a solution of 5 grams of spinacene in 10 c.c. of ether was saturated with hydrogen bromide and allowed to remain for twenty-four hours, the yield of the hydrobromide did not exceed 6·5 grams. When heated, the crystals soften at about 126° and melt to a clear liquid at about 132°. When heated to a still higher temperature, decomposition occurs, hydrogen bromide being freely evolved.

I have devoted a good deal of care to the purification of the hydrochloride and hydrobromide of spinacene, since these compounds are definite and well crystalline, and consequently afford the best indication as to the correct molecular formula of the hydrocarbon. It will be seen that all the results given above agree well with the formula $C_{29}H_{48}$, and although the other derivatives described in my previous communication are less well defined than the hydrogen haloids and not very easily purified, attention may be directed to the fact that, with one exception, the analytical results in all cases agree better with the formula $C_{29}H_{48}$ than with $C_{30}H_{50}$. This will be more clearly seen by reference to the following numbers:

	Found.	$C_{29}H_{48}$.	$C_{30}H_{50}$.
Spinacene trinitrosochloride:			
Cl =	18·48	18·00	17·50
N =	7·36	7·10	6·92
Spinacene trinitrolpiperidide:			
N =	11·52	11·38	11·20
Spinacene trinitrolbenzylamide:			
N =	10·58	10·45	10·27
Spinacene hexanitrosochloride:			
N =	10·62	10·65	10·46
Cl =	27·42	27·00	26·52
Spinacene nitrosate:			
N =	12·80	12·50	12·30

The single exception referred to above is the dodecabromide, which contains Br = 69·7 as compared with 70·79 per cent. required for the lower molecular formula and 70·07 per cent. for the higher. I have already indicated, however, that the action of bromine on

spinacene is very complicated, both addition and substitution derivatives being simultaneously formed. The bromine compound is, moreover, either insoluble or only very sparingly soluble in the great majority of the ordinary organic solvents, and could only be purified by the addition of alcohol to its solution in tetrachloroethane. It is quite possible, therefore, that this compound has not as yet been obtained in a state of purity.

Action of Nitric Acid on Spinacene.

Nitric acid (D 1·42°) mixed with an equal volume of water was added to spinacene and the mixture warmed. A very vigorous reaction occurred with the evolution of oxides of nitrogen. After the reaction had subsided, water was added, and the solid substance which was formed was collected, washed, and dried. It was purified by dissolving it in aqueous sodium hydroxide and by completely saturating the solution with carbon dioxide. The precipitate which formed was separated by filtration, and the clear filtrate, on acidification with dilute sulphuric acid, gave a further precipitate. The latter substance was almost insoluble in ether or petroleum, but moderately soluble in alcohol. It dissolved readily in glacial acetic acid, from which solvent it was obtained by the gradual addition of water as a pale yellow precipitate.

It is clear that in the above experiment at least two products are formed, and doubtless others could be obtained by modifying the conditions of nitration.

Decomposition of Spinacene by Heat in the Presence of Sodium.

At the commencement of this paper, I referred to the fact that a considerable quantity (about 500 c.c.) of spinacene had been distilled over sodium at temperatures corresponding with a pressure of about 45 mm., and that evidence was obtained that under these conditions some decomposition had occurred. The oil which distilled over between 280° and 295°, and measured about 400 c.c., was submitted to fractional distillation (without sodium) under a pressure of about 40 mm. The following four fractions were finally obtained:

(1) 84—88° (about 60 c.c.).
(2) 155—175° (about 60 c.c.).
(3) 220—275° (about 80 c.c.).
(4) 295—298° (about 150 c.c.).

An almost colourless, viscous substance remained in the flask.

The first of the above fractions, which consisted of a fragrant,

mobile liquid, was purified by steam distillation, followed by fractional distillation. The greater portion (about 50 c.c.) boiled constantly at 69°/20 mm.:

0·1097 gave 0·3470 CO_2 and 0·1286 H_2O. C = 86·26; H = 13·02.
0·1121 ,, 0·3555 CO_2 ,, 0·1301 H_2O. C = 86·48; H = 12·89.

From the above, it was clear that this liquid consisted of a hydrocarbon and contained about 0·6 per cent. of oxygen. It was therefore redistilled several times over sodium, and the portion boiling at 51—54°/10 mm. again submitted to analysis:

0·1291 gave 0·4120 CO_2 and 0·150 H_2O. C = 87·02; H = 12·90.
$C_{10}H_{18}$ requires C = 87·0; H = 13·0 per cent.

This hydrocarbon boils under the ordinary pressure at 170—175°, a little polymerisation apparently occurring during the process. It is optically inactive. The following molecular weight determination was made by the cryoscopic method:

0·4021 in 16·36 benzene gave $\Delta^t = -0·909°$. M.W. = 135.
$C_{10}H_{18}$ requires M.W. = 138.

Its specific gravity at 15°/15° = 0·8149 and at 20°/20° = 0·8125.
Its index of refraction at 15° = 1·4588 and at 20° = 1·4565.

Its specific refraction calculated by the $\frac{n^2-1}{(n^2+2)d}$ formula is 0·3353 and the molecular refraction is 46·3.

Taking Conrady's average numbers for the atomic specific refractions (*D*-line), $C_{10}H_{18}$ with one ethenoid linking requires 45·8.

The following estimations were made of the amount of bromine capable of uniting with the hydrocarbon. The bromine was dissolved in carbon tetrachloride and added to a carbon tetrachloride solution of the hydrocarbon under water, the liquid being cooled by means of ice. By working in this way, a correction could be made for the small amount of hydrogen bromide formed as the result of simultaneous substitution. The following are the results of two experiments:

	A.	*B.*
Substance taken	0·1878 gram	0·1348 gram
Bromine uniting with hydrocarbon...	0·2264 ,,	0·1646 ,,

Both these numbers are in close agreement with the addition of two atoms of bromine to one molecule of the hydrocarbon.

All these results point to this substance being a *cyclo*dihydroterpene, and its properties appear to suggest that it may prove to be identical with *cyclo*dihydromyrcene or with *cyclo*linaloolene. It may be of interest to give for purposes of comparison the physical

properties of *cyclo*dihydromyrcene (*Ber.*, 1901, **34**, 3128) and of *cyclo*linaloolene (*Ber.*, 1894, **27**, 2521):

	Hydrocarbon from spinacene.	*cyclo*Dihydromyrcene.	*cyclo*Linaloolene.
Molecular formula	$C_{10}H_{18}$	$C_{10}H_{18}$	$C_{10}H_{18}$
Boiling point	170—175°	169—172°	165—167°
Specific gravity	0·815	0·828	0·811
Refractive index	1·459	1·462	1·460
Number of atoms of bromine added	Two	Two	Two

Had time permitted, specimens of *cyclo*dihydromyrcene and of *cyclo*linaloolene would have been prepared for the purpose of making a fuller comparison. This I hope will be done at some future time. In the above work, steps were taken to make it quite clear that this terpenic hydrocarbon was not formed by the action of sodium on the small amount of oxygenated constituent occurring in the spinacene used. To this end, the spinacene, after having been distilled over a considerable excess of sodium under 10 mm. pressure, was then redistilled over a further quantity of sodium under 40 mm. pressure. From the distillate, the terpenic hydrocarbon described above was separated by steam distillation. The recovered and unchanged spinacene was then for a third time distilled over sodium under 40 mm. pressure, with the result that a further quantity of the terpenic hydrocarbon was obtained. There can, therefore be no reasonable doubt that this *cyclo*dihydroterpene does, in fact, result from the breaking up of the spinacene molecule. The view which I ventured to put forward in my first communication, that spinacene would prove to be related in some way to the terpenes, is therefore correct. The presence in large quantities in fish-liver oil of a complex hydrocarbon closely related to the terpenes is, I think, of very considerable interest both from the chemical and from the physiological points of view. In this connexion, it may be recalled that there is very strong evidence that cholesterol, a substance having nearly the same number of carbon atoms in its molecule as spinacene and occurring also in fish-liver oils, is a complex terpene compound.

The second fraction obtained from the decomposition of spinacene was also a fragrant, tolerably mobile liquid, boiling at 109—115°/10 mm., having an average molecular weight of about 190 and a specific gravity at 15°/15° = 0·868 and at 20°/20° = 0·865. This, as well as the viscous products left in the distillation flask, which doubtless consist of polymerisation products formed during the process, will, it is hoped, be subjected later on to a further study. Except perhaps in one direction in which results of industrial

importance may be anticipated, the further examination of spinacene and its derivatives will have to remain in abeyance until more normal conditions again prevail.

I desire to express my thanks to Miss D. J. Minter and Mr. C. W. McHugo for valuable assistance in connexion with this work.

8 Duke Street,
Aldgate, E.C.3.

[*Received, May 2nd,* 1918.]

XL.—*Metallic Derivatives of Alkaloids.*

By Jitendra Nath Rakshit.

Having prepared the metallic derivatives of acid amides (T, 1913, **103**, 1557) it was thought that the metallic derivatives of alkaloids could be obtained by a similar method. The sodium and potassium derivatives of codeine and narcotine and the sodium derivative of cotarnine were obtained by boiling the alkaloids with the respective metals in benzene, and the calcium derivative of morphine was isolated from the solution of morphine in lime-water or from its alcoholic solution, prepared by titurating morphine with an excess of slaked lime in alcohol. Of the metallic derivatives, those of narcotine require special mention; there is no hydroxyl group present in the molecule, and there is no hydrogen atom attached to the nitrogen that could be displaced by the metals, as is generally represented to be the case with basic or quasi-basic nitrogenous organic compounds.

Sodium Codeine.

A mixture of 200 c.c. of benzene, 5 grams of freshly cut sodium, and 10 grams of powdered anhydrous codeine was boiled under reflux. At the beginning of the experiment, a very faint ammoniacal odour was perceived at the open end of the condenser, and this continued until the end of the operation. Within ten minutes the benzene turned brownish-yellow, and after half an hour it became opaque. After the mixture had boiled for ten hours, the pieces of sodium were covered with a thin layer of a reddish-brown substance, and the boiling was discontinued. On cooling, the contents of the flask set to a viscous mass like brown jelly, which was collected, pressed between filter paper, and kept

over night in a desiccator over sulphuric acid, when it dried tc a brownish-yellow powder:

0·3537 gave 0·0800 Na_2SO_4. Na = 7·32.

$C_{18}H_{20}O_3NNa$ requires Na = 7·18 per cent.

Sodium codeine is readily soluble in water, giving a brownish-yellow, turbid solution which does not become clear by filtration, but the turbidity disappears on the addition of dilute hydrochloric acid, and the colour is also considerably discharged. It is soluble in alcohol, but insoluble in ether, benzene, or chloroform, and is specifically lighter than the last solvent. The compound is slightly deliquescent; on exposure to the air, it absorbs moisture and becomes viscid, but when left in that condition for a long time it does not appear to change. Its aqueous solution does not give any precipitate with Mayer's reagent, but on acidifying the mixture, an immediate curdy, yellow precipitate is obtained.

Potassium Codeine.

Ten grams of dry powdered codeine were dissolved in 200 c.c. of benzene, and the solution was boiled with 10 grams of potassium as before. The potassium melted and formed smaller shining balls, around which a brisk evolution of gas took place. As in the former experiment, a faint ammoniacal odour was always perceived at the open end of the condenser. Within an hour the benzene gradually assumed a reddish-brown colour, and soon afterwards red crystals began to separate. The boiling was continued until a voluminous mass of crystals separated, which were collected, washed three times with boiling benzene, pressed between filter paper, and kept overnight in a desiccator over sulphuric acid. About 5 grams of the substance were powdered, added to 50 c.c. of benzene, and the mixture was gently boiled for five minutes. It was then filtered whilst hot, and the residue washed three times with boiling benzene to remove codeine, being finally pressed between filter paper and dried in a desiccator over sulphuric acid:

0·6000 gave 0·1590 K_2SO_4. K = 11·88.

$C_{18}H_{20}O_3NK$ requires K = 11·59 per cent.

Potassium codeine dissolves in water, giving a clear solution; it is soluble in alcohol, sparingly so in chloroform, and insoluble in ether or benzene.

Sodium Narcotine.

Five grams of narcotine were boiled with 200 c.c. of benzene and 5 grams of clean sodium; a faint ammoniacal odour was per-

ceived, and the colour of the liquid became brown. After boiling for three daily periods of five hours each, some crystals were deposited, which were collected, washed with hot benzene, pressed between filter paper, and kept overnight in a desiccator, when a reddish-yellow powder was obtained:

0·4110 gave 0·7400 Na_2SO_4. Na = 5·82.

$C_{22}H_{22}O_7NNa$ requires Na = 5·41 per cent.

Sodium narcotine is a non-deliquescent substance, readily soluble in water to a pale yellow, transparent solution, which does not produce any precipitate with Mayer's reagent, except on acidification. It is soluble in alcohol or chloroform, and almost insoluble in ether or benzene. Nothing could be extracted from its aqueous solution by benzene or ether. When the solution was boiled, however, a slight turbidity was observed, which increased on passing carbon dioxide; the precipitate was collected, washed, and dried, when it melted at 175°. Narcotine also separated in colourless, needle-shaped crystals when the solution was kept in an open flask for six or seven days, but the alkaloid was completely and readily recovered as a colourless, crystalline powder by dissolving the compound in ammonium chloride. It was collected, washed, dried, and recrystallised from benzene, when it melted at 175° and had all the properties of pure narcotine.

Potassium Narcotine.

In the preparation of other metallic derivatives, excess of the metals were used as a rule, but with the potassium derivative of narcotine considerable difficulty was experienced in obtaining the new compound free from unchanged metal. After a part of the reaction was completed, the molten potassium disintegrated into very small pieces, which were never completely separated from the derivative, but became entangled with the crystals of the new compound and did not settle down separately when cooled. To avoid this difficulty, excess of the alkaloid was employed, and the unchanged narcotine was removed by washing with benzene. Five grams of potassium and 40 grams of narcotine were boiled with 300 c.c. of benzene under reflux. Within an hour the potassium derivative began to be deposited as a brownish-yellow powder. The boiling was continued for twelve hours, during which period the usual faint ammoniacal odour was noticed; the mixture was filtered hot, and the precipitate washed five times with boiling benzene, care being taken to keep it covered with liquid, since the substance rapidly absorbs moisture, becoming nacreous,

and then cannot be filtered; the compound also undergoes slight decomposition. The washing with hot benzene, however, may be continued until the filtrate ceases to give any residue on evaporation. The substance was pressed between filter paper and dried in a desiccator over sulphuric acid:

0·1401 gave 0·0501 K_2SO_4. K = 16·00.

$C_{22}H_{21}O_7NK_2$ requires K = 15·90 per cent.

Dipotassium narcotine is a bright yellow, crystalline powder readily soluble in alcohol, giving a turbid solution; it dissolves in chloroform, is sparingly soluble in benzene, and insoluble in ether. On shaking its aqueous solution with benzene, only a very small quantity of the alkaloid was extracted by the solvent, but when the mixture was shaken with an excess of ammonium chloride, the benzene dissolved almost the whole of the alkaloid. The benzene solution was separated, washed, dried by potassium carbonate, and evaporated, when there remained a non-crystalline residue melting at 160°. Consequently, the substance thus recovered is not pure narcotine, as was the case with the sodium derivative.

Sodium Cotarnine.

Cotarnine was prepared by oxidising narcotine with dilute nitric acid, a slight modification of the method described by Anderson (*Annalen*, 1853, **86**, 187) being used. A mixture of 70 c.c. of nitric acid (D 1·4) and 200 c.c. of water was cooled to 15°, 25 grams of crystallised narcotine were added, and the whole was shaken continuously until the alkaloid was completely dissolved, the solution being kept in a cool place overnight. The white crystals of opianic acid which had settled at the bottom were collected, and the cotarnine was precipitated from the filtrate by means of potassium hydroxide. The alkaloid was well washed, dried in a desiccator over sulphuric acid, and recrystallised from benzene, when it weighed 6·1 grams.

Ten grams of cotarnine, 5 grams of sodium, and 200 c.c. of benzene were heated under reflux; after four hours crystals began to separate, and the boiling was continued for six hours, when the mixture was set aside overnight for the complete precipitation of crystals. These were collected, washed three times with hot benzene, pressed between filter paper, and dried in a desiccator:

0·0130 gave 0·0115 Na_2SO_4. Na = 28·0.

$C_{12}H_{11}O_4NNa_4$ requires Na = 28·30 per cent.

Tetrasodium cotarnine is a hygroscopic, bright yellow, crystalline powder, readily soluble in water, giving a clear solution, soluble

in alcohol or chloroform, sparingly so in ether, and practically insoluble in benzene. This compound showed a behaviour altogether different from that of the allied alkaloids in that its aqueous solution gave a precipitate with Mayer's reagent, the amount of which slightly increased on keeping the solution for a day or on acidifying the freshly prepared solution. When its saturated aqueous solution was treated with an excess of ammonium chloride, an immediate turbidity was observed, and on keeping overnight, a crystalline precipitate had formed. This was collected, washed, pressed between filter paper, and dried in a desiccator over sulphuric acid, when it melted at 132°.

Calcium Morphinate.

Morphine is well known to be soluble in lime-water, forming calcium morphinate, which was easily isolated by the following process. Thirty grams of pure morphine were triturated with 6 grams of pure calcium hydroxide, 100 c.c. of rectified spirit were added, the whole being well mixed for thirty minutes and then filtered. The pale brown filtrate was transferred to a shallow dish and kept in a desiccator over sulphuric acid; after two days, calcium morphinate separated as a shining, scaly, light powder. The product obtained by substituting water for alcohol was not so pure, and was much darker. The alcoholic product was completely dissolved by alcohol or water, whereas the other left a slight residue, and a clear solution was only obtained from it by filtration. Consequently, the alcoholic product was assumed to be pure:

0·2060 gave 0·0200 CaO. Ca = 6·93.

$(C_{17}H_{18}O_3N)_2Ca$ requires Ca = 6·58 per cent.

A quantity of the substance was dissolved in $N/10$-sulphuric acid, and the excess titrated with $N/10$-sodium carbonate, using methyl-orange as indicator.

0·5 required 32·6 c.c. of $N/10$-acid, whereas this weight of a compound of the above formula requires 33·11 c.c. of $N/10$-acid to neutralise both calcium and morphine.

Calcium morphinate is a brown, non-deliquescent powder readily soluble in water or alcohol, sparingly so in chloroform, and insoluble in ether or benzene. Its aqueous solution gives the usual precipitate of morphine with ammonium chloride, and with Mayer's solution it gives a precipitate only after acidification. It is readily decomposed by carbonic acid, calcium carbonate and morphine being precipitated.

The investigation is being extended to the metallic derivatives of other alkaloids and to the study of the constitution of the compounds described above.

The author desires to express his best thanks to the Research Fund Committee of the Chemical Society for a grant which has partly defrayed the cost of the investigation.

Opium Factory,
Ghazipore, India. [*Received, April 10th*, 1917.]

XLI.—*Studies in Catalysis. Part IX. The Calculation in Absolute Measure of Velocity Constants and Equilibrium Constants in Gaseous Systems.*

By William Cudmore McCullagh Lewis.

In previous papers of this series (compare T., 1916, **109**, 796; 1917, **111**, 457), expressions have been obtained, with the aid of the radiation hypothesis, for velocity constants and equilibrium constants as functions of temperature. In the expressions thus obtained, there occur certain proportionality factors which have to be determined by direct comparison with experiment. In the present paper an attempt is made to deal with the problem in a more complete manner by calculating velocity and equilibrium constants in terms of quantities, all of which have a definite physical meaning and may be determined, theoretically, without reference to the actual rate of the chemical reaction itself.

On the basis of statistical considerations, J. Rice (*Rep. Brit. Assoc.*, 1915, 397) has deduced an expression for the reaction velocity and velocity constant in the case of a unimolecular reaction, that is, the spontaneous decomposition of a single molecule. The assumption made by Rice is that the rate of such a reaction is determined by the rate at which the molecules become active in the physical sense. Active molecules, in unimolecular processes, have therefore no real existence. When, however, we deal with multimolecular reactions, it is conceivable that active molecules exist, the rate of the observed reaction depending on the number of collisions per second which take place between active molecules of the participating substances. The concept of active molecules

was first postulated by Arrhenius, but it is only within recent years that the differentiation between active and passive molecules has attained any degree of precision through the introduction of the concept of critical energy and critical increment. The most direct evidence of an experimental kind which we possess at the present time for the existence of active molecules is that afforded by the measurements of Baly and F. O. Rice (T., 1912, **101**, 1475) in the case of the sulphonation of certain aromatic compounds. In this case, the ultimate chemical reaction is multimolecular, probably bimolecular. We may adopt therefore with some confidence the view that active molecules have a real existence in the case of multimolecular reactions. These active molecules differ from the remainder in respect of their internal energy, which is considerably greater than that possessed by an average molecule of the substance at the temperature in question. The fact that the critical energy is high means that only a very small fraction of the total molecules will be active at any moment.

In the case of a bimolecular reaction, such as the decomposition of hydrogen iodide in the gaseous state, the fractional number of hydrogen iodide molecules which exist in the active state may be calculated by the aid of the expression

$$N_a/N = e^{-E/RT} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where N_a denotes the number of active molecules, N the number of passive molecules or the total number of molecules (since N_a is very small compared with N); E is the critical increment reckoned per gram-molecule, that is, the amount of energy which one gram-molecule of the substance must absorb in order to make it reactive, and R and T have their usual significance. This expression is the familiar one obtained on the basis of statistical mechanics for the distribution of molecules in a field of force. The justification for its application to the present case is furnished by the following calculation of the velocity constant of decomposition of gaseous hydrogen iodide.

In Bodenstein's experiments (*Zeitsch. physikal. Chem.*, 1899, **29**, 295), one gram-molecule was present in 22·4 litres. At 556° abs. the observed velocity constant was $9{\cdot}42 \times 10^{-7}$, the unit of time being the minute. On expressing the time in seconds and the concentration in gram-molecules per litre, the velocity constant becomes $3{\cdot}517 \times 10^{-7}$. This number represents the fraction decomposed per second at unit concentration.

We have now to calculate the velocity constant on the basis of the concept of active molecules, the equilibrium concentration of which is assumed to be given at all stages of the observed reaction

by equation (1). From the temperature-coefficient* of the reaction, it is calculated that the critical increment per gram-molecule is 22,000 cals. Hence, employing equation (1), it is found that the fraction of one gram-molecule which exists in the active state at 556° abs. is $2{\cdot}218 \times 10^{-9}$. If there is one gram-molecule of hydrogen iodide present in 1 litre, then this number represents the fractional number of active molecules. Since there are $6{\cdot}1 \times 10^{23}$ molecules in one gram-molecule, the actual number of active molecules per litre is $1{\cdot}35 \times 10^{15}$, or $1{\cdot}35 \times 10^{12}$ per c.c.

On the kinetic theory, the number of collisions per c.c. per second between like (active) molecules is given by the expression

$$\sqrt{2} \cdot \pi \cdot \sigma^2 \cdot u \cdot N_a^2$$

where N_a is the number of active molecules per c.c., u the mean velocity of translation per molecule, and σ the distance within which two molecules approach one another during a collision. Physical theory has not yet succeeded in defining σ with precision, beyond the fact that it is of the order of magnitude of the radius or diameter of the molecule. Such being the case, we shall take a mean value, 2×10^{-8} cm., and employ this in all cases examined. Naturally, this will introduce a certain error into the results, but its magnitude will not affect the general question of the verification of the method of treatment adopted.

In the case of hydrogen iodide at 556° abs., $u = 3{\cdot}3 \times 10^4$ cm. per second. The value of N_a we have already calculated to be $1{\cdot}35 \times 10^{12}$ per c.c. Hence the number of collisions per c.c. per second between the active molecules is $1{\cdot}065 \times 10^{14}$, or the number of collisions per litre is $1{\cdot}065 \times 10^{17}$. At each collision between active molecules, two such molecules react. Hence the number of molecules of hydrogen iodide which react per second per litre is $2{\cdot}13 \times 10^{17}$. Expressing this as a fraction of one gram-molecule, we obtain $2{\cdot}13 \times 10^{17}/6{\cdot}1 \times 10^{23} = 3{\cdot}5 \times 10^{-7}$. This should be the velocity constant of the reaction expressed in gram-molecules per litre per second. The observed value is $3{\cdot}517 \times 10^{-7}$. The agreement is very satisfactory, especially in view of the possible error in σ. This calculation serves to substantiate the concept of active molecules defined in the above sense.

The foregoing calculation may be carried out in a somewhat different manner which leads directly to the differential equation expressing the reaction velocity. Thus the number of molecules which react per c.c. per second is given by:

$$2\sqrt{2}\pi\sigma^2 u N_a^2.$$

* This is the most direct means of obtaining the critical increment. It may also be obtained from the position of the effective absorption band in the spectrum of the substance provided the data are available.

Hence the number of molecules which react per litre per second is given by:

$$2000\sqrt{2}\pi\sigma^2 u N_a^2.$$

N_a is the number of active molecules per c.c. Hence the number of active molecules per litre is 1000 N_a. If N_0 be the number of molecules in one gram-molecule, the number of active gram-molecules per litre is 1000 N_a/N_0. If we denote this by C_a, then $N_a = N_0 C_a/1000$, or $N_a^2 = N_0^2 C_a^2/10^6$. Hence the number of molecules which react per litre per second is:

$$2000\sqrt{2}\pi\sigma^2 u N_0^2 C_a^2/10^{-6}.$$

The number of gram-molecules which react per litre per second is $1/N_0$ of the above quantity. That is, the number of gram-molecules which react per litre per second is

$$2000\sqrt{2}\pi\sigma^2 u N_0 C_a^2/10^6.$$

From equation (1), it follows that $C_a = Ce^{-E/RT}$, where C is the total concentration or number of gram-molecules of hydrogen iodide per litre. Hence the rate of the observed reaction is given by:

$$-dC/dt = 5{\cdot}40 \times 10^{21} . \sigma^2 . u . C^2 . e^{-2E/RT}.$$

But the rate, $-dC/dt = k_{obs.} . C^2$,

where $k_{obs.}$ is the velocity constant experimentally determined. Hence, $k_{obs.}$ (in gram-molecules per litre, per second)

$$= 5{\cdot}40 \times 10^{21} . \sigma^2 . u . e^{-2E/RT} \quad . \quad . \quad . \quad . \quad (2)$$

By making use of the concept of active molecules, we can calculate the velocity constants of decomposition of hydrogen iodide over the temperature range corresponding with Bodenstein's observations. The following table contains the calculated and observed velocity constants expressed in gram-molecules per litre per second.

Decomposition of Hydrogen Iodide.

T.	$u \times 10^{-4}$	Fraction of one gram-molecule in the active state $= e^{-E/RT}$.	$e^{-2E/RT}$.	k calculated [equation (2)].	k observed.
556°	3·30	$2{\cdot}218 \times 10^{-9}$	$4{\cdot}898 \times 10^{-18}$	$3{\cdot}5 \times 10^{-7}$	$3{\cdot}517 \times 10^{-7}$
575	3·356	$2{\cdot}704 \times 10^{-9}$	$1{\cdot}820 \times 10^{-17}$	$1{\cdot}319 \times 10^{-6}$	$1{\cdot}217 \times 10^{-6}$
629	3·510	$2{\cdot}244 \times 10^{-8}$	$5{\cdot}012 \times 10^{-16}$	$3{\cdot}800 \times 10^{-5}$	$3{\cdot}02 \times 10^{-5}$
647	3·559	$3{\cdot}656 \times 10^{-8}$	$1{\cdot}318 \times 10^{-15}$	$10{\cdot}23 \times 10^{-5}$	$8{\cdot}587 \times 10^{-5}$
666	3·612	$5{\cdot}970 \times 10^{-8}$	$3{\cdot}548 \times 10^{-15}$	$2{\cdot}768 \times 10^{-4}$	$2{\cdot}195 \times 10^{-4}$
683	3·657	$8{\cdot}995 \times 10^{-8}$	$8{\cdot}128 \times 10^{-15}$	$6{\cdot}421 \times 10^{-4}$	$5{\cdot}115 \times 10^{-4}$
700	3·702	$1{\cdot}337 \times 10^{-7}$	$1{\cdot}778 \times 10^{-14}$	$1{\cdot}422 \times 10^{-3}$	$1{\cdot}157 \times 10^{-3}$
716	3·744	$1{\cdot}905 \times 10^{-7}$	$3{\cdot}548 \times 10^{-14}$	$2{\cdot}87 \times 10^{-3}$	$2{\cdot}501 \times 10^{-3}$
781	3·912	$6{\cdot}918 \times 10^{-7}$	$4{\cdot}786 \times 10^{-13}$	$4{\cdot}04 \times 10^{-2}$	$3{\cdot}954 \times 10^{-1}$
1000	4·42	$1{\cdot}545 \times 10^{-5}$	$2{\cdot}371 \times 10^{-10}$	22·63	—

The agreement between the observed and calculated values is satisfactory. The number of active molecules per c.c. rises from $1{\cdot}35 \times 10^{12}$ at 556° abs. to $4{\cdot}22 \times 10^{14}$ at 781° abs. Further, it is seen that at 556° abs., when the total concentration is one gram-molecule per litre, the ratio

$$\frac{\text{number of effective collisions per c.c. per second}}{\text{total number of collisions per c.c. per second}} = \frac{1{\cdot}065 \times 10^{14}}{2{\cdot}18 \times 10^{31}} = 4{\cdot}9 \times 10^{-18}.$$

By the term effective collision is meant, of course, the number of collisions between active molecules. This ratio is seen to be an exceedingly small quantity. This quantity may be called conveniently the 'chemical efficiency' of the reaction, since it denotes the number of chemically effective collisions expressed as a fraction of the total number of collisions in the same time. This quantity, as we would expect, increases rapidly with the temperature. Thus, at 781° abs., the chemical efficiency of the reaction considered is $4{\cdot}8 \times 10^{-13}$. At a very high temperature, the upper limit of the efficiency, namely, unity, should be attained theoretically. This temperature must be such that the quantity $e^{-E/RT}$ shall be unity. At 2000° abs., the value of $e^{-E/RT}$ would be $3{\cdot}9 \times 10^{-3}$, and therefore the number of active molecules per c.c., when one gram-molecule is present in one litre, is $2{\cdot}38 \times 10^{18}$. The chemical efficiency is therefore $1{\cdot}5 \times 10^{-5}$. We conclude, therefore, that over any temperature range amenable to experiment in the above reaction the chemical efficiency will be a small quantity.

Bodenstein (*loc. cit.*) has also measured the velocity of union of hydrogen and iodine, and has shown it to be a bimolecular reaction. From the temperature-coefficient, it is easily calculated that the sum of the critical increments per gram-molecule of hydrogen and of iodine is 40,000 cals. This quantity is the analogue of the term $2E$ in the case of the bimolecular decomposition of hydrogen iodide. The quantity 40,000 cals. is made up of two terms, namely, the respective increments of hydrogen and iodine, but at the present stage we do not know each of these terms separately. This is unnecessary, however, for the immediate object in view. It may be noted that the critical increment here referred to is not the critical increment of complete dissociation of hydrogen and of iodine into the atomic state. It will be shown later that the total energy necessary to effect complete dissociation of one gram-molecule of hydrogen and the same mass of iodine is (87,000 + 41,000), or 128,000 cals. The quantity, 40,000 cals., corresponds with a partial activation or polarisation of the hydrogen and iodine molecules sufficient to allow them to react on collision. The partly

activated molecules have a real existence, the system being quite analogous to the partly activated molecules of hydrogen iodide.

On the kinetic theory, the number of collisions per second per c.c. between two unlike molecules is given by the expression:

$$\pi . \sigma^2 . N_1 . N_2 . \sqrt{u_1^2 + u_2^2},$$

where σ is the average distance to which the molecules approach during a collision, u_1 and u_2 are the mean velocities of translation of the two kinds of molecules, and N_1 and N_2 are the number of active molecules of each kind present in unit volume. The value 2×10^{-8} is assigned to σ. Following the same line of argument as that employed in the deduction of equation (2), we find that the bimolecular velocity, expressed in gram-molecules per litre per second, is given by:

$$-dC/dt = 3{\cdot}8 \times 10^{21} \times \sigma^2 \times \sqrt{u_1^2 + u_2^2} \times C_{H_2} . C_{I_2} . e^{-40{,}000/RT}$$

or,

$$k_{obs.} = 3{\cdot}8 \times 10^{21} \times \sigma^2 \times \sqrt{u_1^2 + u_2^2} . e^{-40{,}000/RT} \quad . \quad . \quad (2a)$$

The following table contains the values of the velocity constants calculated by means of equation (2*a*) and those observed by Bodenstein.

Union of Hydrogen and Iodine.

T abs.	$\sqrt{u_1^2 + u_2^2} \times 10^{-4}$	$e^{-40{,}000/RT}$.	k calculated by equation (2*a*).	k observed.
556°	26·5	$1{\cdot}862 \times 10^{-16}$	$7{\cdot}39 \times 10^{-5}$	$4{\cdot}44 \times 10^{-5}$
629	28·2	$1{\cdot}23 \times 10^{-14}$	$5{\cdot}19 \times 10^{-3}$	$2{\cdot}25 \times 10^{-3}$
666	29·0	$7{\cdot}24 \times 10^{-14}$	$3{\cdot}14 \times 10^{-2}$	$1{\cdot}415 \times 10^{-2}$
700	29·7	$3{\cdot}16 \times 10^{-13}$	$14{\cdot}0 \times 10^{-2}$	$6{\cdot}42 \times 10^{-2}$
781	31·4	$6{\cdot}31 \times 10^{-12}$	2·97	1·336

The agreement between observed and calculated values is moderate. The concordance is evidently limited mainly by the degree of approximation in the value taken for σ. In general, the theoretical basis upon which the calculations are founded may be regarded as justified.*

Stegmüller (*Zeitsch. Elektrochem.*, 1910, **16**, 85) has measured, by an electromotive force method, the equilibrium constant of the hydrogen iodide reaction at much lower temperatures than those with which Bodenstein's measurements correspond. By employing equations (2) and (2*a*), it should be possible to calculate the equilibrium constant at any temperature provided the gases do not deviate seriously from the perfect gas. The following table con-

* From the above data it is found that by setting $\sigma = 1{\cdot}34 \times 10^{-8}$ cm. the calculated and observed values of the velocity constants become nearly identical. This value has been employed in the table dealing with Stegmüller's results.

tains the values so calculated and those obtained by Stegmüller. Stegmüller's values have been recalculated to give the equilibrium constant in the form $C_{H_2} \times C_{I_2}/C^2_{HI}$. The velocity constants are expressed in gram-molecules per litre per second.

Equilibrium Constant of the Hydrogen Iodide Reaction at Low Temperatures.

T abs.	Bimolecular velocity constant of decomposition (equation 2).	Bimolecular velocity constant of union (equation 2a) ($\sigma = 1{\cdot}34 \times 10^{-8}$)	Equilibrium constant calculated.	Equilibrium constant, Stegmüller.
304·6°	$1{\cdot}356 \times 10^{-21}$	$2{\cdot}51 \times 10^{-18}$	$5{\cdot}4 \times 10^{-4}$	$11{\cdot}9 \times 10^{-4}$
328·2	$2{\cdot}62 \times 10^{-19}$	$3{\cdot}0 \times 10^{-16}$	$8{\cdot}7 \times 10^{-4}$	$20{\cdot}3 \times 10^{-4}$
354·6	$4{\cdot}123 \times 10^{-17}$	$2{\cdot}98 \times 10^{-14}$	14×10^{-4}	$38{\cdot}3 \times 10^{-4}$

The calculated equilibrium constants are between one-half and one-third of the observed values. Closer agreement is obtained in other reactions, considered later. As illustrated in the above table, we are able to calculate with a moderate degree of accuracy the velocity constants of the opposing reactions, quantities which, owing to their exceedingly small magnitude over the range of temperature considered, could not be determined experimentally.

So far, we have dealt with reaction velocity in gaseous systems from the point of view of molecular statistics. We have now to consider it from the point of view of the radiation hypothesis.

We have seen already that the critical increment of the bimolecular decomposition of hydrogen iodide is 22,000 cals. per gram-molecule. On the radiation hypothesis, this energy is supplied by $N_0 h\nu$ quanta, where N_0 is the number of molecules in one gram-molecule, h is Planck's constant, and ν the frequency of the effective radiation. It is easily calculated that the required frequency is $2{\cdot}33 \times 10^{14}$, or $\lambda = 1{\cdot}3\,\mu$, in round numbers. If the above reasoning is correct, gaseous hydrogen iodide should exhibit an absorption band at this wave-length, especially if the gas be heated. The author is unaware of any experimental data bearing on this point.

On the basis of the quantum theory, Planck has considered the problem of the relation of emission to non-emission by an oscillator (compare Planck, "Theory of Heat Radiation," English trans., p. 164). According to Planck, the ratio of the probability that no emission takes place to the probability that emission does take place is proportional to the radiation density u_ν of the frequency ν. The ratio is given by the expression $p \cdot u_\nu$. The factor p is shown to be identical with the expression $c^3/8\pi h n^3 \nu^3$, where c is

the velocity of light in a vacuum and n the refractive index of the system for the frequency ν. For gaseous systems, n is practically unity. It will be observed that the probability that no emission takes place is inversely as the cube of the frequency. So long as no emission takes place, the energy of the oscillator, and therefore of the whole atom or molecule containing one or more oscillators, remains high. Such a molecule will correspond with an active one in the chemical sense. It is reasonable, therefore, to apply Planck's principle to a case such as the decomposition of hydrogen iodide and write,

$$\frac{\text{the number of chemically active molecules in existence}}{\text{the number of passive molecules}} = p \,.\, u_\nu$$

Since the number of active molecules is exceedingly small, the number of passive molecules is practically identical with the total number present, or, employing the symbols used previously,

$$Na/N = p \,.\, u_\nu.$$

This relation expresses the fact that the higher the radiation density the greater is the number of molecules in the active state. We may also write this expression in the form:

Fraction of one gram-molecule in the active state $= pu_\nu$.

Further, for the short infra-red, visible and ultra-violet regions,

$$u_\nu = \frac{8\pi h n^3 \nu^3}{c^6} e^{-N_0 h\nu/RT},$$

Hence,

$$p \,.\, u_\nu = e^{-N_0 h\nu/RT}$$

or the fraction of one gram-molecule in the active state is $e^{-Nh_0\nu/RT}$ But $N_0 h\nu = E$, the critical increment per gram-molecule. Hence the fraction of one gram-molecule in the active state $= e^{-E/RT}$, which is the expression already obtained on the statistical mechanical basis, and verified by the experimental data. We are justified, therefore, in making the assumption that the chemically active fraction of each gram-molecule of hydrogen iodide is given by the expression $p \,.\, u_\nu$. This should hold good for any substance which reacts in the bimolecular, or in general the multimolecular manner. It is only in such cases that active molecules have any real existence. In the case of unimolecular reactions, active molecules do not exist as such.

In a bimolecular reaction of the type considered, if C denotes the total number of gram-molecules in a given volume, say 1 litre, then the number of active gram-molecules in the same volume may be expressed by

$$C \,.\, p \,.\, u_\nu \text{ or } C \,.\, e^{-N_0 h\nu/RT} \text{ or } C \,.\, e^{-E/RT}$$

On the purely kinetic basis, we have seen that the rate of reaction between like molecules in a bimolecular reaction per litre per second is:

$$-dC/dt = 5{\cdot}4 \times 10^{21} \cdot \sigma^2 \cdot u \cdot C^2 e^{-2E/RT}.$$

The term $C^2 \cdot e^{-2E/RT}$ is evidently identical with $C^2 \cdot p^2 \cdot u_\nu^2$, so that the rate of reaction may be written,

$$-dC/dt = 5{\cdot}4 \times 10^{21} \cdot \sigma^2 \cdot u \cdot p^2 \cdot C^2 \cdot u_\nu^2.$$

That is, the rate of the observed bimolecular reaction depends on the square of the radiation density, a conclusion which is in agreement with the assumption made in earlier papers in connexion with bimolecular reactions. The advantage of the present mode of treatment is, however, that all the factors which go to make up the observed velocity constant are calculable quantities. It is evident that the observed velocity constant, expressed in gram-molecules per litre per second, for a bimolecular reaction involving like molecules is given by:

$$k_{\text{obs.}} = 5{\cdot}4 \times 10^{21} \cdot \sigma^2 \cdot u \cdot p^2 \cdot u_\nu^2,$$

or

$$k_{\text{obs.}} = 5{\cdot}4 \times 10^{21} \cdot \sigma^2 \cdot u \cdot e^{-2N_0 h\nu/RT}.$$

It is obvious that differentiation of this expression with respect to temperature yields the well-known Arrhenius equation as a first approximation.

In a bimolecular reaction such as that considered, the function of the radiation of the absorbable type is to maintain a certain number of molecules in the chemically active state, a state which means high energy content. The number of active molecules at any moment is the difference between their rate of production and their rate of disappearance. Their rate of disappearance is due to retransformation of some into the passive state, and at the same time the transformation of others in the ordinary chemical sense into the resultants. It is simply the number of active gram-molecules *in existence* at any moment which has been written as $C \cdot p \cdot u_\nu$. The actual rate of production of active molecules per second is a quantity necessarily much greater than this. An attempt will now be made to estimate this rate.

In the case of hydrogen iodide at a concentration of one gram-molecule per litre at 556° abs., we have seen that the number of active molecules maintained by the radiation in the active state per litre is $1{\cdot}35 \times 10^{15}$. The number of active molecules which react per second per litre is $2{\cdot}13 \times 10^{17}$. If we denote by R_1 the rate of production of active molecules per second per litre, by R_2 the rate of chemical reaction ($2{\cdot}13 \times 10^{17}$), and by R_3 the rate at

which active molecules are retransformed into passive molecules per litre per second, we have the relation:

$$R_1-(R_2+R_3)=1{\cdot}35\times10^{15}.$$

In order to maintain the active molecules and allow for the rate of the observed reaction, the minimum rate of production of active from passive molecules is $>2{\cdot}13\times10^{17}$. The true rate may, however, be much greater than this lower limit. It is evident that the rate of production of active molecules must depend on the radiation density u_ν, but it is evident the rate is not given by the expression $N_0 . p . u_\nu$, for this would only account for a production of $1{\cdot}35\times10^{15}$ active molecules per second from one gram-molecule. A quantity having a higher numerical value than $N_0 . p . u_\nu$ is required. The terms N_0 and u_ν would be expected to remain unaltered, and we are limited to some function of p. It will be shown later, in connexion with the dissociation of iodine, bromine, and chlorine, that the experimental values can be accounted for if we assume provisionally that the required function is 10^3p^2.* With this assumption, the rate of production of active molecules from one gram-molecule is $N_0 . 10^3 . p^2 . u_\nu$. Since u_ν itself can be written as $\frac{1}{p}e^{-N_0h\nu/RT}$, our assumption means that the rate of production of active molecules is given by $10^3 . N_0 . pe^{-N_0h\nu/RT}$, or $10^3 . N_0 . p . e^{-E/RT}$. This expression should be the correct one for any spontaneous unimolecular reaction, for in such a case the process of activation is identical with the chemical reaction. That is, the velocity constant of a unimolecular reaction should be given by:

$$k_{\text{obs.}}=10^3 . p . e^{-E/RT}$$

We shall now apply this expression to the calculation of the rate of production of active molecules of hydrogen iodide. The term p is given by $c^3/8\pi h n^3\nu^3$, and since, for the process considered, $E=N_0h\nu=22{,}000$ cals. per gram-molecule, the frequency ν must be $2{\cdot}33\times10^{14}$. Further, the system is gaseous, and therefore the refractive index is practically unity. Hence $p=1{\cdot}307\times10^{13}$. Hence the number of active molecules produced per second from one gram-molecule of hydrogen iodide at 556° abs. $=6{\cdot}1\times10^{23}\times 1{\cdot}307\times10^{13}\times2{\cdot}218\times10^{-9}=1{\cdot}768\times10^{28}$. If we divide this number by $6{\cdot}1\times10^{23}$, we obtain the fraction of one gram-molecule activated per second. A rate of this magnitude is quite possible in the sense that it is sufficient to account for the observed rate of the

* This function will be dealt with in a later paper, in which an alternative expression, having a similar numerical value, but possessing a more precise physical significance, will be given.

bimolecular reaction, and likewise for the maintenance of the free active molecules. Since the rate of production of active molecules is considerably greater than the sum of the two effects just mentioned, it follows that the rate at which active molecules are retransformed into passive is likewise of the order 10^{28}. If these extremely high opposing velocities exist, we are led to the conclusion that the equilibrium between active and passive molecules is attained practically instantaneously. This is in agreement with experience, but, of course, such evidence is very inconclusive. Quantitative evidence is furnished by the calculation of the equilibrium constant in the case of the dissociation of iodine, bromine, and chlorine. This will be considered later.

Whilst the ordinary thermal decomposition of hydrogen iodide is a bimolecular process, Bodenstein has shown (*Zeitsch. physikal. Chem.*, 1907, **61**, 447) that the photochemical decomposition is unimolecular. In this case, the process is the decomposition of hydrogen iodide molecules into atoms of hydrogen and iodine. This is effected by short waves. That is, the process of completely decomposing the hydrogen iodide molecule is a much more difficult one to carry out and requires a greater size of quantum than is required simply to displace the atoms somewhat with respect to one another inside the hydrogen iodide molecule, thereby permitting the bimolecular process to take place. In Bodenstein's experiments on the photochemical decomposition, the hydrogen iodide was exposed to bright sunlight in glass vessels. Berthelot and Gaudechon (*Compt. rend.*, 1913, **156**, 889) find that hydrogen iodide is decomposed by blue or violet light. More precise knowledge is wanting, but it is evident that the active wave-length is of the order $450\,\mu\mu$, or $\nu = 6{\cdot}66 \times 10^{14}$. That is, the critical increment E' per gram-molecule of hydrogen iodide for the unimolecular decomposition is 63,000 cals. in round numbers. It will be shown later that a more exact value for this quantity is 66,000 cals. This is just three times the increment for the bimolecular reaction. The bimolecular reaction takes place, therefore, more readily, since a molecule will oftener possess the energy corresponding with E than the energy corresponding with E'. This unimolecular process must take place, however, as a thermal effect along with the bimolecular process, for, at any temperature, the radiation density, even at $\nu = 7{\cdot}0 \times 10^{14}$, cannot be entirely wanting. Since, however, the radiation density diminishes rapidly as the frequency increases from the short infra-red into the ultra-violet, the unimolecular reaction, compared with the bimolecular, will remain negligible until very high temperatures are reached. On the basis of the considerations already developed, it is quite possible to calculate what this uni-

molecular decomposition velocity amounts to at any temperature. Thus, the rate of unimolecular decomposition of hydrogen iodide per gram-molecule is given by $10^3 . N_0 . p . e^{-66,000/RT}$, where $p = 4{\cdot}66 \times 10^{11}$. At 556° abs., this rate should be $3{\cdot}12 \times 10^{12}$ molecules per second when one gram-molecule is present initially. Hence the unimolecular velocity constant $= 10^3 . p . e^{-66,000/RT}$ is $5{\cdot}1 \times 10^{-12}$. It will be observed that this is a small quantity compared with the bimolecular velocity constant ($3{\cdot}5 \times 10^{-7}$) under the same conditions. At 781° abs., the unimolecular velocity constant is $1{\cdot}54 \times 10^{-4}$, whilst the bimolecular constant is $4{\cdot}0 \times 10^{-2}$. The conclusion that the unimolecular decomposition is small compared with the bimolecular over the range examined by Bodenstein (556—781° abs.) is in agreement with the fact that the bimolecular formula holds good. We can easily calculate the bimolecular constant at 1000° abs. by the methods already employed at lower temperatures, the value obtained being 22·63. At the same temperature, the unimolecular velocity constant is calculated to be 1·73. At 1200° abs., the unimolecular constant is 435, whilst the bimolecular is 998. It is evident, therefore, that at a temperature somewhat above 1200° abs., the two types of decomposition will occur at the same rate. At this temperature, therefore, the bimolecular formula would be expected to break down.

We now turn to the consideration of unimolecular dissociation, such as that of iodine in the gaseous state into atoms. From the known behaviour of nascent atoms, it may be inferred that their normal state in respect of energy content is sensibly identical with the critical state, so that the exponential term in equation (2) containing the critical increment reduces to unity. Let C_u denote the equilibrium concentration of undissociated molecules of iodine expressed in gram-molecules per litre, and C_i the equilibrium concentration of the iodine atoms in the same units. The rate at which the molecular species dissociates is then given by $C_u . 10^3 . p . e^{-N_0 h\nu/RT}$ or $C_u . 10^3 . p . e^{-E/RT}$. In an earlier paper (T., 1917, **111**, 1086), the value 41,000 cals., per gram-molecule, has been assigned to the critical increment of iodine. The corresponding frequency ν is $4{\cdot}3 \times 10^{14}$, or $\lambda = 700\ \mu\mu$. Hence $p = c^3/8\pi h\nu^3 = 2{\cdot}08 \times 10^{12}$. At $T = 1073$ ($t° = 800°$), the term $e^{-E/RT} = 4{\cdot}385 \times 10^{-9}$. Hence the rate of dissociation, expressed in gram-molecules per litre per second, is $C_u \times 10^3 \times 2{\cdot}08 \times 10^{12} \times 4{\cdot}385 \times 10^{-9} = 9{\cdot}16 \times 10^6 C_u$. The number $9{\cdot}16 \times 10^6$ is the unimolecular velocity constant of dissociation. The rate at which the atoms combine is given by the total collision frequency, for in the case considered, the atoms are all active and every collision is effective. Since there are C_i gram-atoms per litre, the actual number of atoms per c.c. is

$C_i \times 6{\cdot}1 \times 10^{20}$. The collision frequency per c.c. per second is $\sqrt{2} \cdot \pi \cdot u \cdot \sigma^2 \cdot C_i^2 \times 37{\cdot}2 \times 10^{40}$. The average velocity of translation u of one iodine atom at 1073° abs. is $4{\cdot}6 \times 10^4$ cm. per second. Taking σ as 2×10^{-8} cm., the number of collisions per c.c. per second is $3{\cdot}031 \times 10^{31} \cdot C_i^2$. The number of atoms which combine is just twice this quantity, namely, $6{\cdot}062 \times 10^{31} \cdot C_i^2$. Hence the number of *gram*-atoms which combine per second per litre is $9{\cdot}94 \times 10^{10} \cdot C_i^2$. Alternatively, using equation (2) and writing the exponential term as unity, we arrive at the same result. It follows that $C_i^2/C_u = 9{\cdot}16 \times 10^6/9{\cdot}94 \times 10^{10} = 9{\cdot}2 \times 10^{-5}$. Bodenstein and Starck (*Zeitsch. Elektrochem.*, 1910, **16**, 961) have measured the equilibrium constant, C_i^2/C_u, at 1073° abs., with the concentration expressed in gram-molecules per litre, the value obtained being $1{\cdot}29 \times 10^{-4}$. The calculated equilibrium constant agrees well with the observed value. Again, consider the dissociation at 1473° abs. The value of $e^{-E/RT}$ is $8{\cdot}166 \times 10^{-7}$. Hence the rate of dissociation in gram-molecules per second is

$$2{\cdot}08 \times 10^{15} \times 8{\cdot}166 \times 10^{-7}\ C_u.$$

From equation (2), taking σ as 2×10^{-8} and $u = 5{\cdot}38 \times 10^4$, we get for the rate of union of the atoms, expressed in gram-atoms per litre per second, the value $1{\cdot}14 \times 10^{11} \times C_i^2$. Hence

$$C_i^2/C_u = 1{\cdot}699 \times 10^9/1{\cdot}14 \times 10^{11} = 1{\cdot}49 \times 10^{-2}.$$

The observed equilibrium constant is $1{\cdot}02 \times 10^{-2}$.

The foregoing considerations, which are based partly on molecular statistics and partly on the quantum theory of radiation, allow us to calculate with a moderate degree of precision not only the equilibrium constant of a dissociation of a molecule into atoms (a quantity which is amenable in general to experimental determination), but likewise the separate velocity constants which, owing to their great magnitude, cannot be measured directly. The table on p. 484 contains the values of the equilibrium constants and the velocity constants in the above units for the dissociation of iodine over the range of temperature investigated by Bodenstein and Starck.

The agreement between the calculated and observed equilibrium constants is satisfactory. This affords considerable support for the assumptions made as regards the velocity constants. It may be pointed out that the term $e^{-E/RT}$ in this case does *not* represent the number of the active molecules of molecular iodine. No active molecules exist apart from the atoms. The conditions obtaining are quite distinct from those met with in the case of the bimolecular decomposition of hydrogen iodide.

Bodenstein (*Zeitsch. Elektrochem.*, 1916, **22**, 327) has measured

Dissociation of Iodine.

t°.	T abs.	$e^{-E/RT}$.	Mean velocity of translation of an iodine atom in cm. per sec. × 10^{-4}.	Unimolecular velocity constant of dissociation.	Bimolecular velocity constant of recombination.	Equilibrium constant (calculated).	Equilibrium constant (observed).
800	1,073°	$4{\cdot}385 \times 10^{-9}$	4·6	$9{\cdot}16 \times 10^{6}$	$9{\cdot}94 \times 10^{10}$	$9{\cdot}2 \times 10^{-5}$	$1{\cdot}29 \times 10^{-4}$
900	1,173	$2{\cdot}265 \times 10^{-8}$	4·83	$4{\cdot}71 \times 10^{7}$	$1{\cdot}04 \times 10^{11}$	$4{\cdot}5 \times 10^{-4}$	$4{\cdot}92 \times 10^{-4}$
1,000	1,273·	$8{\cdot}995 \times 10^{-8}$	5·058	$1{\cdot}87 \times 10^{8}$	$1{\cdot}08 \times 10^{11}$	$1{\cdot}7 \times 10^{-3}$	$1{\cdot}58 \times 10^{-3}$
1,100	1,373	$2{\cdot}944 \times 10^{-7}$	5·24	$6{\cdot}12 \times 10^{8}$	$1{\cdot}13 \times 10^{11}$	$5{\cdot}4 \times 10^{-3}$	$4{\cdot}37 \times 10^{-3}$
1,200	1,473	$8{\cdot}166 \times 10^{-7}$	5·38	$1{\cdot}69 \times 10^{9}$	$1{\cdot}14 \times 10^{11}$	$1{\cdot}49 \times 10^{-2}$	$1{\cdot}02 \times 10^{-2}$

the dissociation constant of gaseous bromine between 800° and 1200°. He finds that the equilibrium constant, expressed in partial pressure terms, is given by the expression:

$$\log K_p = -10100/T + 1{\cdot}75 \log T - 0{\cdot}000409T + 4{\cdot}726 \times 10^{-8}T^2 + 0{\cdot}548.$$

Further details are not given in the abstract, which alone is available. At 1000° abs., this expression gives $\log K_p = \bar{5}{\cdot}336$, whence the equilibrium constant K_c, expressed in gram-molecules per litre, is $2{\cdot}64 \times 10^{-7}$.

An attempt will now be made to calculate this equilibrium constant. The critical increment E per gram-molecule of bromine is not known with accuracy (compare T., 1917, **111**, 1086). It may be taken to be of the order 50,000 cals. The corresponding frequency $\nu = 5{\cdot}3 \times 10^{14}$. Hence $p = 1{\cdot}1 \times 10^{12}$ and

$$e^{-E/RT} = 1{\cdot}175 \times 10^{-11}.$$

At the equilibrium point, the rate of dissociation of the bromine molecules is $10^3 \,.\, p \,.\, C_u \;\; e^{-E/RT} = 10^3 \times 1{\cdot}1 \times 10^{12} \times 1{\cdot}175 \times 10^{-11} \times C_u = 1{\cdot}29 \times 10^4 C_u$, where $1{\cdot}29 \times 10^4$ is the calculated unimolecular velocity constant of decomposition and C_u is the number of gram-molecules per litre. In dealing with the union of the atoms, we shall again make the assumption that the atoms are all active. At 1000° abs., the average speed u of a bromine atom is $5{\cdot}6 \times 10^4$ cm. per second. Setting $\sigma = 2{\cdot}0 \times 10^{-8}$ cm., and employing equation (2), we obtain for the rate of union of the atoms per second per litre the value $1{\cdot}21 \times 10^{11} C_i^2$, where the numerical coefficient is the bimolecular velocity constant. The equilibrium constant is therefore given by $C_i^2/C_u = 1{\cdot}29 \times 10^4 / 1{\cdot}21 \times 10^{11} = 1{\cdot}0 \times 10^{-7}$. This agrees satisfactorily with the observed value when we consider the possible error in σ and in E.*

The dissociation of chlorine has been measured by Pier (*Zeitsch. physikal. Chem.*, 1908, **62**, 417), but the values appear to be much less accurate than those of Bodenstein in the case of bromine and iodine. Thus, the heat of the reaction when calculated from successive values of the equilibrium constant varies in quite an unexpected manner with the temperature. As the possibility of error seems to be less in the higher temperature range, we shall restrict ourselves to this region. Thus, at 1940° abs., the observed degree of dissociation of chlorine is 0·0157, the pressure being 0·5 atmosphere. Hence $K_c = x^2/(1-x)V = 7{\cdot}8 \times 10^{-7}$. The critical increment of chlorine is taken to be 86,000 cals. per gram-molecule

[1] In the paper referred to, E for bromine was taken to be 57,000 cals. per gram-molecule. Employing the value 50,000 cals., the calculated heat of formation of potassium bromide is in rather better agreement, and the heat of formation of silver bromide in rather worse agreement with the corresponding observed value than are the numbers given in the former paper.

(compare T., 1917, **111**, 1086). Hence at 1940° abs., $e^{-E/RT} = 2{\cdot}014 \times 10^{-10}$. The frequency $\nu = 9{\cdot}1 \times 10^{14}$. Hence $p = 2{\cdot}2 \times 10^{11}$. At the equilibrium point, the rate of dissociation of chlorine is consequently $4{\cdot}43 \times 10^4 C_u$, where $4{\cdot}43 \times 10^4$ is the unimolecular velocity constant expressed in gram-molecules per second. The average speed u of a chlorine atom at 1940° abs. is $8{\cdot}3 \times 10^4$ cm. per second. Taking σ as $2{\cdot}0 \times 10^{-8}$ cm., and using equation (2), we obtain, for the rate of union of the atoms, $1{\cdot}793 \times 10^{11} C_i^2$, the velocity constant being expressed in gram-molecules per litre per second. Hence the equilibrium constant, C_i^2/C_u should be $4{\cdot}43 \times 10^4 / 1{\cdot}793 \times 10^{11}$, or $2{\cdot}47 \times 10^{-7}$. It will be seen that the calculated and observed values of the equilibrium constant are of the same order of magnitude. The results obtained in the case of the three halogens, iodine, bromine, and chlorine, afford a considerable amount of evidence in favour of the theoretical treatment employed.

In the type of reaction just considered, namely, the dissociation of a molecule into atoms in the gaseous state, the position of equilibrium is given by the relation:

$$10^3 . p . e^{-E/RT} . C_u = 5{\cdot}40 \times 10^{21} . \sigma^2 . u . C_i^2 \quad . \quad . \quad (3)$$

or

$$K = C_i^2/C_u = \frac{10^3 p . e^{-E/RT}}{5{\cdot}40 \times 10^{21} . \sigma^2 . u}$$

where the concentration is expressed in gram-molecules per litre. In a gaseous system p may be written as $1{\cdot}6 \times 10^{56}/v^3$, where v is the frequency of the radiation responsible for the dissociation process. For a given substance, v is a constant independent of temperature so long as the mechanism of the process remains the same. We can write the above expression in the form:

$$\log K = -E/RT - \log u + \log 10^3 . p/5.40 \times 10^{21} \times \sigma^2.$$

The final term on the right-hand side is analogous to the integration constant which occurs in the thermodynamic treatment of mass-action equilibrium. In the present case, however, the final term is calculable quite apart from the reaction itself. On differentiating the above expression with respect to temperature, we obtain:

$$d \log K / dT = E / RT^2 - d \log u / dT.$$

The mean velocity of translation of an atom (which has been taken as practically identical with the root-mean-square-velocity) is proportional to the square root of the absolute temperature, u being given by the expression $\sqrt{3RT/M}$, where M is the gram-molecular weight of the atom. Hence

$$d \log K / dT = (E - 1/2 . RT)/RT^2.$$

The term $(1/2)RT$ is, in general, small compared with E, and therefore the critical increment in the case of reactions of the above type is practically identical with the heat of dissociation at constant volume. This is the assumption which has been made in the foregoing treatment. If $-Q_v$ denotes the heat absorbed at constant volume per gram-molecule dissociated, we obtain the van't Hoff isochore from the above expression. For the type of reaction considered, the exact relation between the critical increment and the heat of the reaction is given by:

$$-Q_v = E - 1/2 \,.\, RT \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

We are now in a position to deal with the dissociation of hydrogen. Langmuir (*J. Amer. Chem. Soc.*, 1915, **37**, 417) finds that the heat of dissociation at constant volume at 3000° abs. is 84,000 cals. per gram-molecule. Hence, from equation (4), we obtain 87,000 cals. as the critical increment per gram-molecule of hydrogen. The corresponding frequency is $9{\cdot}21 \times 10^{14}$, or $\lambda = 325\ \mu\mu$. Hence $p = 2{\cdot}04 \times 10^{11}$. At 2000° abs., $e^{-E/RT} = 3{\cdot}055 \times 10^{-10}$. Hence the rate of dissociation $= 10^3 \,.\, p \,.\, e^{-E/RT} \,.\, C_u = 6{\cdot}23 \times 10^4 C_u$. At 2000° abs., u for one hydrogen atom is $7{\cdot}1 \times 10^5$ cm. per second. Taking $\sigma = 2 \times 10^{-8}$ cm., and using equation (2), the rate of union of hydrogen atoms, assuming all the atoms active, is $1{\cdot}53 \times 10^{12} C_i^2$, the velocity constant being expressed in gram-atoms per litre per second. Hence the equilibrium constant is $4{\cdot}07 \times 10^{-8}$. The degree of dissociation of hydrogen as determined by Langmuir is 0·0033 at 2000° abs. and under one atmosphere's pressure. Hence Langmuir's equilibrium constant, expressed in concentration terms, is $6{\cdot}6 \times 10^{-8}$. This agrees fairly well with the calculated value. The main cause of the discrepancy is probably the fact that in the case of the hydrogen atom, σ is less than 2×10^{-8} cm. If we set $\sigma = 1{\cdot}57 \times 10^{-7}$ cm., the two values of the equilibrium constant become identical. This value of is used in the following table, which contains the values of K obtained by Langmuir and those obtained by the above method of calculation.

Dissociation of Hydrogen.

T abs.	u in cm. per sec. $\times 10^{-5}$	Unimolecular velocity constant of dissociation.	Bimolecular velocity constant of union.	Equilibrium constant, calculated.	Equilibrium constant, Langmuir.
1,500°	6·15	41·66	$8{\cdot}2 \times 10^{11}$	$5{\cdot}1 \times 10^{-11}$	$4{\cdot}6 \times 10^{-11}$
2,000	7·1	$6{\cdot}23 \times 10^4$	$9{\cdot}4 \times 10^{11}$	$[6{\cdot}6 \times 10^{-8}]$	$6{\cdot}6 \times 10^{-8}$
2,500	7·95	$4{\cdot}98 \times 10^6$	$1{\cdot}1 \times 10^{12}$	$4{\cdot}7 \times 10^{-6}$	$5{\cdot}1 \times 10^{-6}$
3,000	8·66	$9{\cdot}26 \times 10^7$	$1{\cdot}2 \times 10^{12}$	$8{\cdot}0 \times 10^{-5}$	$7{\cdot}0 \times 10^{-5}$
3,500	9·37	$7{\cdot}46 \times 10^8$	$1{\cdot}3 \times 10^{12}$	$6{\cdot}0 \times 10^{-4}$	$6{\cdot}1 \times 10^{-4}$
4,000	10·0	$3{\cdot}58 \times 10^9$	$1{\cdot}33 \times 10^{12}$	$2{\cdot}7 \times 10^{-3}$	$2{\cdot}9 \times 10^{-3}$

The agreement throughout is satisfactory. It should be observed, however, that both series of K values are dependent on the numerical value for the heat effect, namely, 84,000 cals. at constant volume. This quantity has been verified approximately by Isnardi (*Zeitsch. Elektrochem.*, 1915, **21**, 405).

The following considerations also afford some support in favour of Langmuir's value for Q_v. We have seen that when hydrogen iodide decomposes in the *uni*molecular manner, the critical increment E' is approximately 63,000 cals. per gram-molecule. Let us suppose that two gram-molecules decompose in this manner, not in the ordinary bimolecular manner. That is, we have the reactions:

$$2HI \longrightarrow 2H + 2I \longrightarrow H_2 + I_2.$$

This will be referred to as the 'atomic' process. Although this is formally the same as the ordinary bimolecular process, the actual mechanism, involving as it does the formation of free atoms, is different, for in the bimolecular process we deal only with a polarisation or partial activation of each of the molecules H_2, I_2, and HI, a process which requires much less energy to reach the respective critical states than is required for the actual dissociation of each molecular species into atoms. Every chemical process, occurring spontaneously, follows the path of least resistance, that is, the path involving minimal critical increments. Hence the atomic process referred to is not the naturally occurring one. Since, however, the chemical change as a whole is the same in the two cases, the total heat effect must be the same. The heat absorbed when two gram-molecules of hydrogen iodide decompose is 4000 cals. approximately. Applying the expression developed and tested in former papers, namely,

$$\text{heat evolved} = (E_{\text{resultants}} - E_{\text{reactants}}),$$

to the above atomic process, we obtain:

$$-4000 = E_{H_2} + E_{I_2} - 2E'_{HI}.$$

The symbol E_{I_2}, which is the critical increment of dissociation of iodine into its atoms, has the value 41,000 cals. per gram-molecule. $2 \times E'_{HI} = 2 \times 63{,}000$ cals. Hence the quantity E_{H_2}, which denotes the critical increment of dissociation of one gram-molecule of hydrogen into its atoms, has the value 81,000 cals. This should be sensibly identical with the heat absorbed in the dissociation of hydrogen. It is seen to be in fair agreement with Langmuir's value. The source of the discrepancy is due mainly to error in the value of E'_{HI}, which we have taken to be 63,000 cals. per gram-molecule on the basis of the rather qualitative statement

made by Berthelot and Gaudechon that hydrogen iodide is decomposed by blue or violet light. If we take the critical increment of hydrogen, in respect of dissociation into atoms, to be 87,000 cals. per gram-molecule (the value which has been employed in the compilation of the above table), it follows from a consideration of the atomic process of the decomposition of hydrogen iodide that E'_{HI} should be 66,000 cals., this being the quantity required to dissociate one gram-molecule of the substance into free atoms of hydrogen and iodine. From what has been said, this may be regarded as a more exact value of the critical increment of unimolecular decomposition than the value 63,000 cals. Certain conclusions have been drawn from this as regards the relative speeds of the unimolecular and bimolecular decompositions of hydrogen iodide in an earlier part of this paper. A further conclusion is that gaseous hydrogen iodide, when heated, should exhibit an absorption band in the region of $\nu = 7 \times 10^{14}$, or $\lambda = 429\,\mu\mu$. The author is unaware of any measurements in this connexion.

The decomposition of hydrogen iodide is particularly interesting, because it is one that is capable of occurring in two distinct ways, namely, the unimolecular and the bimolecular, and, if the previous considerations be accepted, we have fairly complete information regarding the mechanism of both. In the case of the ordinary bimolecular decomposition of hydrogen iodide, the critical increment E per gram-molecule is 22,000 cals. This is just one-third of the critical increment E′, 66,000 cals., which is required for the complete dissociation of the molecule into free atoms. The ordinary bimolecular process occurs, therefore, with much greater ease, that is, at lower temperatures, than does the unimolecular process. The bimolecular process involves, therefore, a certain separation or polarisation of the atoms in the molecule, but not their complete separation. The bimolecular process may be represented in the following manner, in which an additive compound is formed:

$$2HI \longrightarrow \begin{matrix} H\text{—}I \\ \vdots \quad \vdots \\ H\text{—}I \end{matrix} \longrightarrow \begin{matrix} H\cdots\cdots I \\ | \quad | \\ H\cdots\cdots I \end{matrix} \longrightarrow H_2 + I_2.$$

The total amount of energy required to activate two gram-molecules of hydrogen iodide in this manner is 44,000 cals.

In conclusion, we may collect together the various numerical values for the critical increments of the substances dealt with in the present paper.

Substance (gaseous).	Critical increment in cals. per gram-molecule.	Reaction involving the critical increment of the previous column.
Hydrogen iodide	22,000	$2HI \rightarrow H_2 + I_2$ ordinary bimolecular reaction.
Hydrogen iodide	66,000	$HI \rightarrow H + I$ unimolecular reaction, identical with the photochemical decomposition.
Hydrogen	87,000	$H_2 \rightarrow 2H$.
Iodine	41,000	$I_2 \rightarrow 2I$.
Bromine	50 000	$Br_2 \rightarrow 2Br$.
Chlorine	86,000	$Cl_2 \rightarrow 2Cl$.

Summary.

(1) The observed rate of a unimolecular reaction is identical with the rate at which the molecules pass from the passive to the active state per second. The active state differs from the passive in respect of internal energy. The activation is ascribed to the radiation density of the absorbable radiation. In unimolecular reactions, active molecules have no real existence. They are, in fact, the resultants of the reaction. The critical increment E, that is, the quantity of energy which must be added to an average gram-molecule to raise its energy content to the critical state, is given by the expression $N_0 h\nu$, where h is Planck's constant, ν the frequency of the absorbable radiation, and N_0 the number of molecules in one gram-molecule. This statement is simply Einstein's law of the photochemical equivalent.

If the concentration of the decomposing substance is C, the provisional expression for the rate of decomposition in a unimolecular process is:

$$-dC/dt = 10^3 . p . C . e^{-E/RT},$$

where $p = c^3/8\pi h n^3 \nu^3$, c being the velocity of light in a vacuum and n the refractive index of the system for the frequency ν. In the case of gaseous systems, $n = 1$ very nearly, and $p = 1{\cdot}6 \times 10^{56}/\nu^3$. It follows that the observed velocity constant of a unimolecular process is given by:

$$k_{obs.} = 10^3 p . e^{-E/RT}.$$

Alternatively, the rate of unimolecular decomposition is given by:

$$-dC/dt = 10^3 . p^2 . C u_\nu,$$

where u_ν is the radiation density of the effective frequency ν, the radiation density being determined by the temperature of the system.

(2) The rate of a bimolecular reaction is identical with the

number of collisions which occur per second between the active molecules. As already pointed out in the case of *uni*molecular reactions, active molecules have no real existence. In bimolecular and multimolecular reactions generally, active molecules exist, their rate of formation being very much greater than their rate of collision, which latter term defines the observed rate of reaction. The number of active molecules in existence at any moment is proportional to the radiation density. In multimolecular reactions, the fraction of one gram-molecule existing in the active state is given on the basis of molecular statistics by the expression $e^{-E/RT}$, where E is the critical increment per gram-molecule. The fraction of one gram-molecule existing in the active state is given on the radiation basis by pu_ν, which is identical with $e^{-N_0h\nu/RT}$ and therefore with $e^{-E/RT}$. If C is the total concentration in gram-molecules per litre, the number of active gram-molecules per litre is $C \cdot e^{-E/RT}$. The number of "effective" collisions which occur in a gaseous system between like molecules (such as molecules of hydrogen iodide) per c.c. per second is given on the molecular kinetic theory by the expression,

$$\sqrt{2} \cdot \pi \cdot u \cdot \sigma^2 \cdot (\text{number of active molecules per c.c.})^2,$$

where u is the average velocity of translation of a molecule at the temperature considered and σ is the range of approach of two molecules during a collision. At each collision between active molecules, two molecules react. Hence the rate of reaction in a bimolecular process between like molecules occurring in the gaseous state is given by:

$$-dC/dt = 5{\cdot}40 \times 10^{21} \cdot u \cdot \sigma^2 \cdot C^2 \cdot e^{-E/RT}.$$

Alternatively, since $e^{-2E/RT} = p^2 \cdot u_\nu^2$, the rate of reaction may be written:

$$-dC/dt = 5{\cdot}40 \times 10^{21} \times u \times \sigma^2 \times p^2 \times u_\nu^2 \times C^2.$$

The observed bimolecular velocity constant, for a reaction between molecules of the same kind (expressed in gram-molecules per litre per second), is given by:

$$k_{\text{obs.}} = 5{\cdot}40 \times 10^{21} \cdot u \cdot \sigma^2 \cdot e^{-2E/RT}$$

or

$$k_{\text{obs.}} = 5{\cdot}40 \times 10^{21} \cdot u \cdot \sigma^2 \cdot p^2 \cdot u_\nu^2.$$

If the reaction occurs between molecules of different kinds, for example, the union of hydrogen and iodine, the velocity constant is given by:

$$k_{\text{obs.}} = 3{\cdot}8 \times 10^{21} \cdot \sigma^2 \cdot \sqrt{u_1^2 + u_2^2} \cdot e^{-(E_1+E_2)/RT}.$$

where u_1 and u_2 are the average velocities of translation of the two kinds of molecules, E_1 is the critical increment of the one kind (per gram-molecule), and E_2 is the corresponding quantity for the other kind. When the bimolecular reaction occurs between nascent atoms, all the reactants are normally in the reactive state, and therefore the exponential term reduces to unity. In such a case, for example, the combination of atoms to form the undissociated molecule of a gas, the bimolecular velocity constant is given by the expression:

$$k = 5{\cdot}40 \times 10^{21} \,.\, u \,.\, \sigma^2.$$

(3) The various statements made in (1) and (2) are borne out quantitatively in the cases examined, namely, the decomposition of hydrogen iodide (bimolecular reaction), the union of hydrogen and iodine molecules, and the dissociation of iodine, bromine, chlorine, and hydrogen gases. It is shown that the opposing velocity constants, as well as the equilibrium constants, can be calculated in regions in which, owing to the rate being either extremely great or extremely small, the chemical change cannot be determined experimentally.

(4) The velocity constant of *uni*molecular decomposition of gaseous hydrogen iodide has been calculated at various temperatures, and is shown to be negligible compared with the bimolecular constant over the range of temperature examined by Bodenstein. In the neighbourhood of 1200° abs., it is calculated that the two velocity constants should be of the same order of magnitude, and therefore the ordinary bimolecular expression should fail to apply quantitatively.

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[*Received, April 22nd*, 1918.]

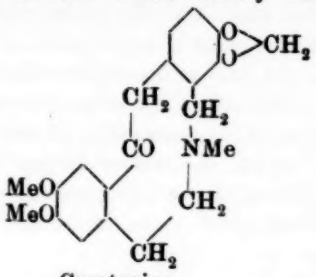
XLII.—epi*Berberine*.

By WILLIAM HENRY PERKIN, jun.

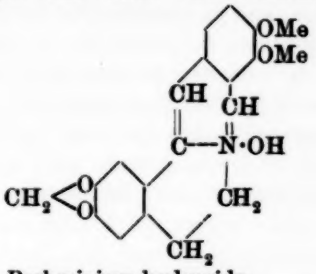
DURING the discussion of the results of an experimental investigation into the constitution of cryptopine, it was pointed out (T., 1916, **109**, 833) that the comparison of the formula of this substance with that of berberinium hydroxide* shows that these

* The nomenclature employed in this communication is clearly set out on p. 503.

substances are related in a very striking manner, and this relationship is still more clearly brought out when the formulæ of

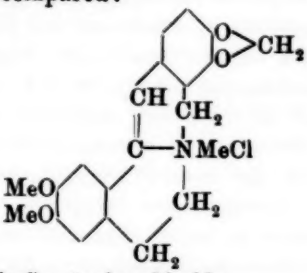


Cryptopine.

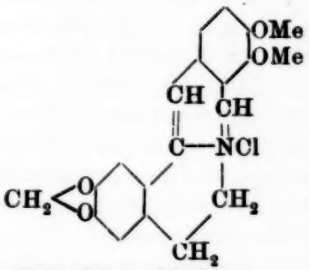


Berberinium hydroxide.

*iso*cryptopine chloride and berberinium chloride (*loc. cit.*, p. 833) are compared:



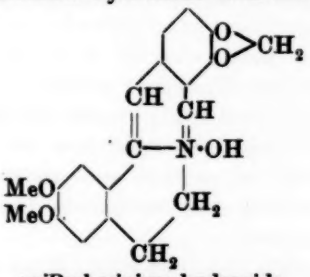
*iso*Cryptopine chloride.



Berberinium chloride.

The difference in constitution between the two alkaloids and the two salts is essentially due, first, to the presence of the *N*-methyl group in cryptopine and its absence in the berberine molecule, and, secondly, to the fact that, whereas the four oxygen atoms attached to the two benzene nuclei and carrying the methylene and the two methyl groups, are in the same position in each formula, in the case of cryptopine, the methylenedioxy-group is in the upper and the two methoxy-groups in the lower part of the molecule, whilst in berberinium hydroxide the positions are reversed.

In other words, cryptopine is related to an alkaloid isomeric with ordinary berberinium hydroxide and having the constitution



*epi*Berberinium hydroxide

and it is this substance which has been named epi*berberinium hydroxide*. This substance has, so far, not been met with in nature, and it appeared to the author that it would be an interesting problem to endeavour to prepare it, and thus to be in a position to compare its properties and the properties of its salts with those of berberinium hydroxide and its salts. In order to obtain *epi*berberinium salts from cryptopine, it was essential, in the first place, to discover some method by which the methyl group could be detached from the nitrogen atom in the cryptopine molecule, and this proved to be an undertaking of more than ordinary difficulty.

After several unsuccessful attempts in which various condensing and oxidising agents were employed, the most hopeful course seemed to be the application of a method for removing alkyl groups from nitrogen, which had been discovered by Diels and his pupils (Diels and Fritzsche, *Ber.*, 1911, **44**, 3020; Diels and Paquin, *ibid.*, 1913, **46**, 2000). These investigators have shown that, whereas azodicarboxylic ester, $CO_2Et{\cdot}N{:}N{\cdot}CO_2Et$, combines with primary amines to yield amides, it forms additive compounds with secondary and tertiary amines which are readily hydrolysed by dilute hydrochloric acid, yielding hydrazo-ester together with aldehydes and amines. The important point is that the amines thus formed contain one radicle less than the secondary or tertiary amine employed in the first instance. Thus azodicarboxylic ester combines with dimethylamine to yield the substance,

$$CO_2Et{\cdot}N(CH_2{\cdot}NHMe)NH{\cdot}CO_2Et,$$

and this is hydrolysed by dilute hydrochloric acid into hydrazodicarboxylic ester, formaldehyde, and methylamine:

$$CO_2Et{\cdot}N(CH_2{\cdot}CHMe)NH{\cdot}CO_2Et + H_2O = CO_2Et{\cdot}NH{\cdot}NH{\cdot}CO_2Et + CH_2O + NH_2Me.$$

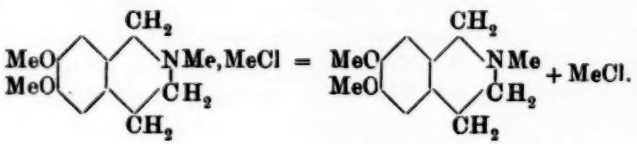
Subsequently, Diels and Ernst Fischer (*Ber.*, 1914, **47**, 2043) showed that *N*-methylpiperidine and complex substances such as atropine, morphine, and codeine could be demethylated by treatment with azodicarboxylic ester followed by hydrolysis with dilute hydrochloric acid.

As there seemed no reason why the same process might not lead to the elimination of the *N*-methyl group in cryptopine, a large number of experiments were made on the action of azodicarboxylic ester on the alkaloid under the conditions recommended by Diels and Fischer in the case of codeine and under various other conditions, including heating the substances together without dilution with a neutral solvent.

In no single case could the formation of an additive product be

observed, and most of the cryptopine was always recovered unchanged when the product of the action was boiled with dilute hydrochloric acid. It is not improbable that this negative result is due, in part at least, to the fact that cryptopine, unlike the alkaloids employed by Diels and Fischer, is very sparingly soluble in boiling acetone and other suitable solvents and also in azodicarboxylic ester, and thus intimate contact with the latter cannot be brought about.

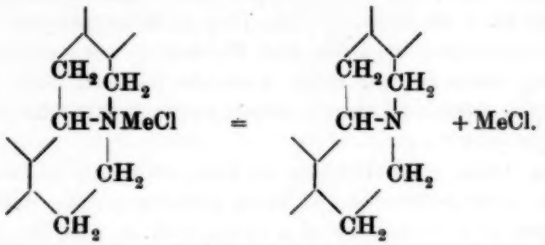
During these experiments, it was noticed that many methochlorides decompose, often at their melting points, with the evolution of gas and formation of a froth, and it was the inquiry into the meaning of this decomposition which ultimately led to the discovery of a process for preparing derivatives of *epi*berberine. One of the first substances to be investigated was 6:7-dimethoxy-2-methyltetrahydro*iso*quinoline methochloride (see below), because it happened to be available. This substance (1 gram) was placed in a test-tube, the upper part of which was drawn out to a long capillary, and the tube heated in a sulphuric acid bath, when decomposition occurred at about 270°, and, on applying a light to the end of the capillary, the issuing gas burnt with a green-edged flame and was at once recognised as methyl chloride. When effervescence had ceased, the residue was distilled under diminished pressure, and passed over as a colourless syrup which solidified to crystals melting at 83°. This substance was 6:7-dimethoxy-2-methyltetrahydro*iso*quinoline, so that decomposition had taken place according to the scheme:



In order to investigate a case approximating more closely to that of cryptopine, berberine was converted into tetrahydroanhydroberberine (tetrahydroberberine), and this into tetrahydroanhydroberberine methochloride (compare Pyman, T., 1913, **103**, 828).

The β-modification of this methochloride was heated in a drawn-out test-tube in a sulphuric acid bath exactly as described above, and again yielded methyl chloride and a dark brown syrup, but this change did not take place until the temperature had reached 285—290°. Less decomposition of the product occurred when the process was carried out under 10 mm. pressure. The residual brown mass separated from alcohol in leaflets which melted at

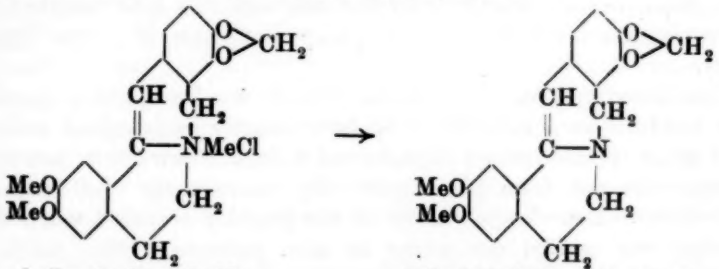
169—171°, and consisted of tetrahydroanhydroberberine, elimination of methyl chloride having occurred according to the partial scheme:



It remained now to apply this method to the quaternary chlorides derived from cryptopine, but, when this was done, great difficulties were at once encountered because of the very high temperatures which are required in order to bring about scission even under diminished pressure.

Indeed, in some of the cases investigated, the temperature necessary to cause elimination of methyl chloride is considerably above the point of decomposition of the product. In such circumstances, the isolation of any of the product is only possible when quite small quantities of material are decomposed at any one time and the experiment is rapidly carried out. The yield, even under the most favourable conditions, is then only a small one, and the preparation of any quantity of material for subsequent examination consequently a very tedious operation.

The case most exhaustively studied in the cryptopine series has been that of *iso*cryptopine chloride (T., 1916, **109**, 883), because this is by far the most accessible of the quaternary chlorides derived from this alkaloid. When *iso*cryptopine chloride, in quantities of 1 gram, is heated under diminished pressure, elimination of methyl chloride occurs at about 260°, and it has been found possible to isolate from the black residue, by employing one of the methods described on p. 506, a pure substance which on examination has been found to be *dihydroanhydro*epi*berberine*:

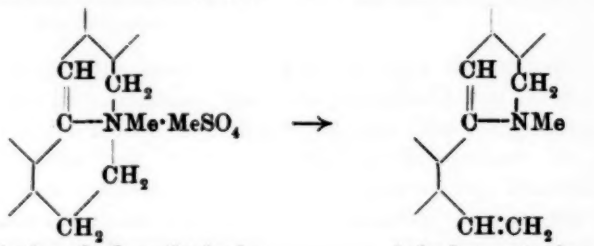


*iso*Cryptopine chloride. Dihydroanhydro*epi*berberine.

Dihydroanhydroepiberberine, $C_{20}H_{19}O_4N$, resembles dihydroanhydroberberine * in appearance and in many of its other properties. It melts at 170—172°, separates from acetone in iridescent, golden plates, and yields a very sparingly soluble hydrochloride,

$$C_{20}H_{19}O_4N,HCl,3H_2O,$$

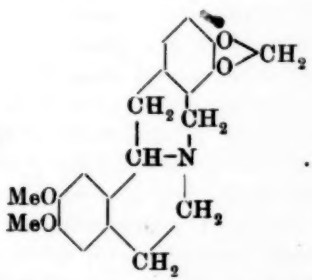
which crystallises in deep yellow, prismatic needles. Dihydroanhydroberberine melts at 170—172°, separates from acetone in yellow prisms, and is also characterised by the sparing solubility of its hydrochloride, $C_{20}H_{19}O_4N,HCl,3H_2O$, and other salts which, like the salts of dihydroanhydro*epi*berberine, are all bright yellow or orange. Dihydroanhydro*epi*berberine combines with methyl sulphate to yield the methosulphate, $C_{20}H_{19}O_4N,Me_2SO_4$, which crystallises splendidly in yellow prisms, and when boiled with methyl-alcoholic potassium hydroxide is readily decomposed with



Dihydroanhydro*epi*berberine methosulphate. Anhydrocryptopine.

separation of anhydrocryptopine (T., 1916, **109**, 975), a decomposition which is a welcome confirmation of the constitution assigned to dihydroanhydro*epi*berberine.

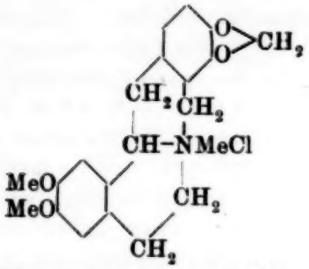
Tetrahydroanhydroepiberberine,



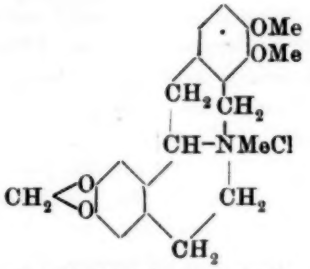
During the course of the investigation of cryptopine, $C_{21}H_{23}O_5N$, it was discovered that this alkaloid is reduced by sodium amalgam with the formation of dihydrocryptopine, $C_{21}H_{25}O_5N$, and this tertiary base, under the influence of acetyl chloride, is converted

* A detailed investigation of this substance is nearly completed, and will, it is hoped, shortly be ready for publication.

into two stereoisomeric quaternary chlorides, $C_{21}H_{24}O_4NCl$, which were named the α- and β-chlorides of *iso*dihydrocryptopine (T., 1916, **109**, 839). The close relationship between these chlorides and tetrahydroanhydroberberine methochloride was commented on



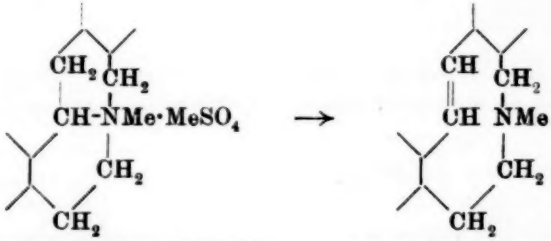
*iso*Dihydrocryptopine chloride.



Tetrahydroanhydroberberine methochloride.

at the time, as was also the fact that these substances are the counterpart of one another in all their reactions. It has already been mentioned (p. 495) that tetrahydroanhydroberberine β-methochloride is decomposed on heating with the elimination of methyl chloride and formation of tetrahydroanhydroberberine, and it therefore seemed probable that a similar decomposition would take place in the case of *iso*dihydrocryptopine chloride and result in the formation of *tetrahydroanhydroepiberberine*. The first experiments in this direction were disappointing, because the only chloride available was the β-modification, and this does not lose methyl chloride until nearly 300°, and then not readily, with the result that much decomposition of the product occurs. The α-modification of the methochloride is unfortunately very difficult to obtain, since it is produced only in very small quantity during the action of acetyl chloride on dihydrocryptopine. However, a small quantity of the quite pure α-chloride was prepared and found to decompose, when heated under diminished pressure, at a much lower temperature than the β-modification, namely, at about 230°, and the dark-coloured residue could then be purified by the methods given on p. 511, and yields *tetrahydroanhydroepiberberine*. This substance separates from alcohol in colourless needles, and not in the stout prisms so characteristic of tetrahydroanhydroberberine, but in other respects it resembles the latter in a remarkable degree. It melts at the same temperature (170—171°) and yields exactly similar, very sparingly soluble salts, of which the hydrochloride, $C_{20}H_{21}O_4N,HCl$, for example, is almost insoluble in dilute hydrochloric acid. It was subsequently found that tetrahydroanhydro*epi*berberine may be obtained from dihydroanhydro*epi*berberine by

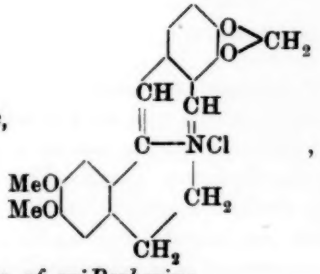
reduction with zinc or tin and hydrochloric acid, and this observation made it possible to prepare enough material for the detailed examination of this interesting substance. It is a strong base, combines readily with methyl sulphate in the cold, yielding *tetrahydroanhydroepiberberine methosulphate*, a colourless, crystalline substance which is decomposed by boiling with methyl-alcoholic potassium hydroxide, with the formation of anhydrodihydro-



Tetrahydroanhydro*epi*berberine methosulphate. Anhydrodihydrocryptopine. (*A*)

cryptopine (*A*) (compare T., 1916, **109**, 938).

epi*Berberinium Chloride*,

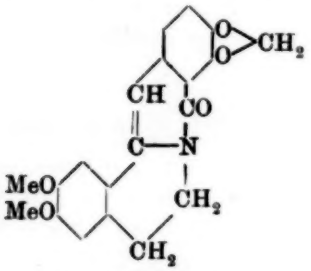


and other Salts of epi*Berberine*.

The magnificent, deep orange salts of *epi*berberine may be obtained either from dihydroanhydro*epi*berberine or tetrahydroanhydro*epi*berberine by the action of such oxidising agents as iodine or dilute nitric acid, but are best prepared from these bases by boiling with mercuric acetate in acetic acid solution, a process recommended by Gadamer (*Arch. Pharm.*, 1915, **253**, 274) in the case of the oxidation of dihydro- and tetrahydro-anhydroberberine to the corresponding berberinium salts. Thus, when dihydroanhydro*epi*berberine, dissolved in acetic acid, is boiled with mercuric acetate, mercurous acetate separates, and if this is removed by filtration and hydrochloric acid added to the filtrate, epi*berberinium chloride* separates. This salt crystallises from water in glistening, deep orange needles which are deeper in colour than the

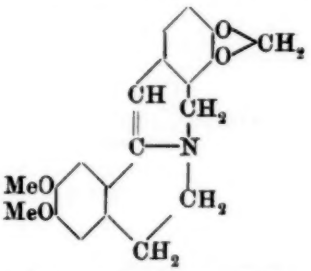
crystals of berberinium chloride, and it is remarkable that the composition of the salt, $C_{20}H_{18}O_4NCl,4H_2O$, is the same as that of berberinium chloride, and that, on heating, it behaves exactly like the latter and loses $3H_2O$ readily, but the remaining H_2O with much greater difficulty. The *sulphate*, *iodide*, and *nitrate* are also intensely coloured salts, and the picrate melts at 222°, whereas berberine picrate melts at 239—240° (Pictet and Gams, *Ber.*, 1911, **44**, 2485).

The Action of Sodium Hydroxide on epi*Berberinium Sulphate. Formation of Oxy*epi*berberine and Dihydroanhydro*epi*berberine.*



Oxy*epi*berberine.

and



Dihydroanhydro*epi*berberine.

The remarkable conversion of berberinium sulphate into a mixture of oxyberberine and dihydroanhydroberberine by the action of sodium hydroxide at the temperature of the water-bath was first observed by Gadamer (*Arch. Pharm.*, 1905, **243**, 34), and when the same process was applied to *epi*berberinium sulphate, it was found that not only did the reaction proceed in the same direction, but the conversion was even more quantitative than in the case of the berberinium salt. The dihydroanhydro*epi*berberine obtained was compared with the dihydroanhydro*epi*berberine which results from the action of heat on *iso*cryptopine chloride (p. 506), and the two preparations were found to be identical.

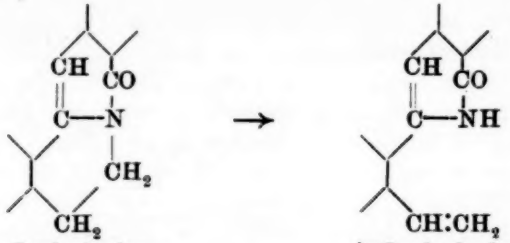
*Oxy*epi*berberine*, $C_{20}H_{17}O_5N$, melts at 240—241°, and has properties which are very similar to those of oxyberberine (m. p. 198—200°). Both are feeble bases and crystallise from acetic acid in the form of their beautifully crystalline acetates,

$$C_{20}H_{17}O_5N,C_2H_4O_2,$$

which are dissociated by water or when they are heated at 80—90° into acetic acid and oxy-berberine or *-epi*berberine.

When oxyberberine is heated in a sealed tube with dilute hydrochloric acid at 130°, it gradually undergoes isomeric change and

yields *iso*oxyberberine, the conversion taking place in the following direction:

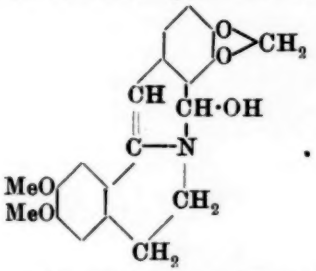


Oxyberberine. *iso*Oxyberberine.

(Perkin and Robinson, T., 1912, **101**, 262). This curious process does not take place at 130° in the case of oxy*epi*berberine, but is rapid and quantitative at about 150—160°. iso*Oxy*epi*berberine*, like the corresponding berberine derivative, is practically devoid of basic properties; it does not melt at 300°, and is even more sparingly soluble in the usual solvents than *iso*oxyberberine (m. p. 245°), but it may be recrystallised from pyridine.

The alkaloid, berberine, $C_{20}H_{19}O_5N$, was first isolated by Gadamer (*Arch. Pharm.*, 1905, **243**, 33), who obtained it by adding a large excess of sodium hydroxide to berberinium hydroxide (or the sulphate) and extracting with ether. It crystallises from ether in yellow needles and melts at 144°.

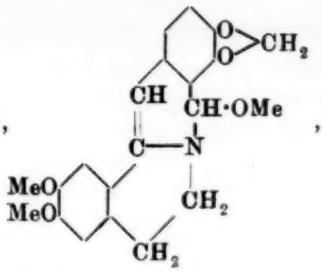
During the course of this investigation, experiments on the action of sodium hydroxide on *epi*berberine sulphate were made under the conditions recommended by Gadamer in the hope that it might prove possible to isolate epi*berberine*,



These were, however, only partly successful, since the *epi*berberine, which was obviously formed, could not be isolated in a pure condition.

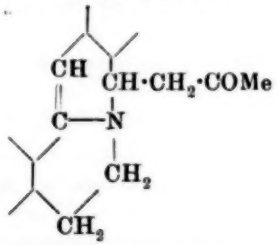
The substance always contained oxy*epi*berberine, which seems to be produced as the result of oxidation even when the ethereal solution of *epi*berberine remains in contact with air. On the other hand, the *O*-methyl and *O*-ethyl derivatives have been obtained in a pure condition.

O-*Methyl*epi*berberine*,



and O-*Ethyl*epi*berberine*.

G. M. and R. Robinson (T., 1917, **111**, 967) have recently shown that berberine is converted by treatment with methyl alcohol in the cold into *O*-methylberberine (methoxydihydroberberine), and the corresponding ethyl derivative is obtained when ethyl alcohol is employed. The present author finds that these substances are more conveniently prepared by the action of sodium methoxide or ethoxide on berberinium sulphate, and hopes shortly to publish the details of these and other experiments on several new derivatives of berberine. *O*-Methyl and *O*-ethyl derivatives of *epi*berberine are obtained under exactly similar conditions. Thus *epi*berberinium chloride (or the sulphate) yields, on treatment in methyl-alcoholic suspension with sodium methoxide, O-*methyl*epi*berberine*, $C_{20}H_{18}O_4(OMe)N$, which separates from methylal in splendid brownish-yellow prisms and melts at 150—152°. The corresponding O-*ethyl* derivative does not crystallise so readily and melts at 135—136°. Both these substances dissolve in boiling dilute hydrochloric acid, and, on cooling, *epi*berberinium chloride separates. They also dissolve readily in boiling acetone, and when the solution is concentrated and set aside, *anhydro*epi*berberine-acetone*, $C_{20}H_{17}O_4N,C_3H_6O$, separates. This interesting substance, which doubtless contains the grouping



melts at 162°, crystallises in yellow prisms, and is, in appearance and properties, exactly analogous to anhydroberberine-acetone (m. p. 175°), which is similarly produced when *O*-methyl- or *O*-ethyl-berberine is dissolved in boiling acetone.

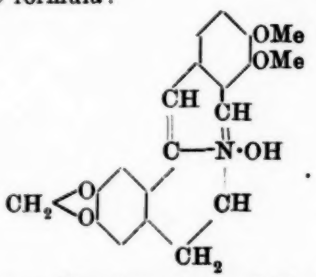
The Nomenclature of Berberine and its Salts.

During the last few years, some difficult points connected with the constitution of berberine and its salts, which still remained, have been definitely cleared up, and it seems to the author that a system of nomenclature should now be adopted which is in accordance with the new views. There can be no doubt that the alkaloid exists in two distinct modifications, one of which is crystalline and the other so far known only in solution. When a solution of the sulphate is mixed with the quantity of barium hydroxide necessary for the removal of the sulphuric acid, the filtered solution is strongly alkaline, and a similar alkaline solution is obtained when superheated steam is passed into anhydroberberine-acetone,

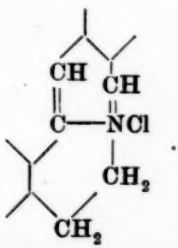
$$C_{20}H_{17}O_4N,C_3H_6O$$

(Gadamer, *Arch. Pharm.*, 1905, **243**, 33).

Unfortunately, it has not been found possible to isolate this soluble alkaline modification of the alkaloid, since decomposition occurs during evaporation even at the ordinary temperature in a vacuum desiccator, but it is now generally recognised that this alkaline solution contains the ammonium hydroxide modification represented by the formula:



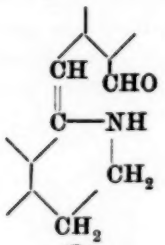
It is clear that this modification, from which the salts are obtained by the replacement of the hydroxyl group by acid radicles, may conveniently and correctly be termed *berberinium hydroxide*. The salt commonly known as berberine hydrochloride is, of course, not a hydrochloride, but a quaternary chloride containing the grouping



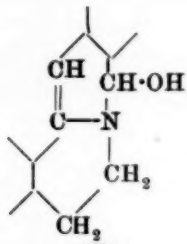
and must therefore be named *berberinium chloride*.

The solid modification of the alkaloid was first isolated by Gadamer (*loc. cit.*, p. 33), who obtained it by adding a large excess of sodium hydroxide to the aqueous solution of berberinium hydroxide, or the sulphate, and extracting with ether. It crystallises from ether in yellow needles, melts at 144°, and has the composition $C_{20}H_{19}O_5N$.

Owing to the fact that this modification yielded oxyberberine and dihydroberberine on treatment with hot concentrated sodium hydroxide solution, and therefore behaved like an aromatic aldehyde, Gadamer considered that the substance was an aldehyde of the formula I, and he therefore named it "berberinal." On the other hand, Tinkler (T., 1911, **99**, 1345) was led to the conclusion that "the evidence obtained from the spectroscopic examination of berberinal points to the fact that the substance is not the aldehydic (I), but the carbinol modification (II) of the alkaloid:



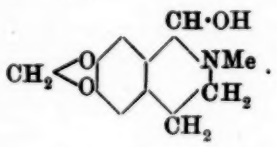
(I.)



(II.)

."

In a paper, published in 1912, on the exhaustive methylation of tetrahydroanhydroberberine (McDavid, Perkin, and Robinson, T., **101**, 1219), the carbinol formula for the alkaloid was accepted, and recently (T., 1917, **111**, 958) G. M. and R. Robinson adopted the same view, mainly as the result of a comparison of the behaviour of berberinal and cotarnine,

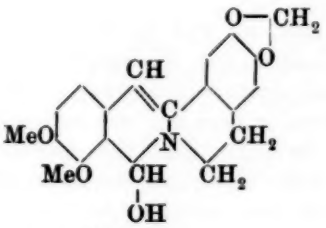


towards acetone, alcohols, amides, and other substances, with which both bases yield similarly constituted and highly characteristic condensation products. Since berberinal is obtained by the action of alkali on the salts of berberine, and on the other hand is converted into the salts of berberine by solution in acids, it appears to the author that it should, in future, be called "berberine," a plan which would do away with the anomaly

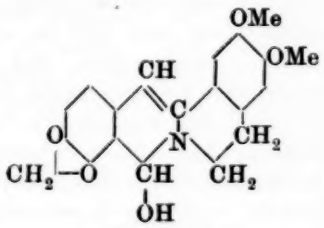
that, whereas the salts of berberine are recognised, there is, at the present time, no berberine corresponding with them. The quaternary salts of berberine, which are derived from berberinium hydroxide, should, then, be called "berberinium salts," so, for example, berberinium chloride, $C_{20}H_{18}O_4NCl$, nitrate, $C_{20}H_{18}O_4N,NO_3$, etc. The adoption of this system of nomenclature necessitates a change in the names of the reduction products derived from berberine. The substances called dihydroberberine, $C_{20}H_{19}O_4N$, and tetrahydroberberine, $C_{20}H_{21}O_4N$, are not direct reduction products of berberine, $C_{20}H_{19}O_5N$, but are derived from the alkaloid by reduction and simultaneous removal of the elements of water. Their names must therefore be altered to *dihydroanhydroberberine* and *tetrahydroanhydroberberine* respectively. Acetoneberberine, $C_{20}H_{18}(CH_2{\cdot}COMe)O_4N$, is formed from berberine by condensation with acetone, with the elimination of water, and should therefore be named anhydroberberineacetone, when its relationship to anhydrocotarnineacetone is at once recognised.

It is clear that the similar condensation products of berberine with 2-methylindole, acetophenone, *cyclo*hexanone, etc. (compare G. M. and R. Robinson, T., 1917, **111**, 959), are also anhydroberberine derivatives.

It may be pointed out that the actual placing of the berberine formulæ in the present communication has been employed in order to bring out clearly the similarity in constitution between cryptopine and berberine or *epi*berberine, but, for most purposes, there is much to be said in favour of writing the formulæ for berberine and *epi*berberine in the following manner:



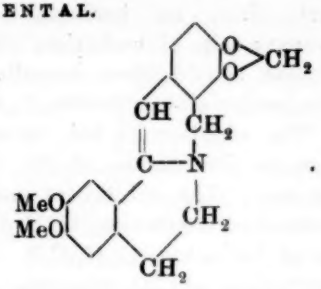
Berberine.



*epi*Berberine.

Experimental.

Dihydroanhydroepiberberine,



This substance is obtained, as explained on p. 496, when *iso*cryptopine chloride is heated, and it is important that the chloride employed should be quite free from cryptopine hydrochloride, that is, that it should give no precipitate when its aqueous solution is made alkaline with ammonia and boiled.* If any cryptopine hydrochloride is present, much decomposition occurs during the heating, and the product is, of course, contaminated with cryptopine, and consequently difficult to purify.

The finely powdered and sieved chloride, after being carefully dried in the steam-oven, is placed, in quantities of not more than 2 grams, in a wide test-tube fitted with a cork and bent tube, the whole connected with a good water pump, and exhausted to, at the most, 15 mm. The test-tube, placed in a metal-bath, is gradually heated until any moisture has been removed, the temperature is then raised, rather rapidly, to 220°, during which the powder darkens in colour, and is apt to be projected about the test-tube and into the bent delivery tube.

Decomposition soon sets in, with frothing and formation of a dark brown, viscous mass, and, so soon as the disengagement of methyl chloride becomes rapid, the temperature is allowed to drop to 200—205°, and kept at this for three or four minutes and until the frothing has almost subsided. In order that the operation may be successful, the decomposition must be carried out as rapidly as possible, and the experiment requires considerable practice. The hot tube is allowed to cool slightly and then plunged into

* *iso*Cryptopine chloride, prepared by the action of phosphoryl chloride on cryptopine (T. 1916, **109**, 883) frequently contains traces of cryptopine hydrochloride. When this is the case, the whole is dissolved in boiling water, the solution made alkaline with ammonia, heated on the water-bath for some minutes and then filtered from the trace of cryptopine. The filtrate, on keeping, deposits a voluminous precipitate of pure *iso*cryptopine chloride. This quaternary salt dissolves moderately readily in boiling glacial acetic acid, and separates well as a voluminous mass of colourless groups of needles, a method which yields the salt in an exceptionally pure state.

water so that the resin may crack, become detached from the sides of the tube, and easily rubbed off with a glass rod; otherwise, if the tube is allowed to cool slowly, the resin becomes very firmly attached and is most difficult to scrape off. The crude, dark brown product may then be treated in two different ways in order to extract the dihydroanhydro*epi*berberine.

(1) The resin is dissolved in hot dilute acetic acid (25 per cent.), the dark brown solution precipitated with ammonia, the gelatinous precipitate immediately extracted with much ether, and the ethereal solution decanted or rapidly filtered from the troublesome slimy precipitate, which consists largely of unchanged *iso*cryptopine chloride. After drying over potassium carbonate, filtering, and concentrating, the ethereal solution is left in the ice-chest, when it gradually deposits a brick-red, crystalline precipitate which, after collecting and washing with ether, consists of almost pure dihydroanhydro*epi*berberine. This substance may be obtained quite pure by repeating the solution in dilute acetic acid, precipitation with ammonia, and extraction with ether, or it may be crystallised from methyl alcohol or acetone (see below).

(2) The finely powdered resin is boiled with water, which extracts unchanged *iso*cryptopine chloride and a dark reddish-brown impurity, the precipitate is collected by the aid of the pump, and washed with hot water until the filtrate is no longer red. The residue, after draining on porous porcelain, is triturated with methyl alcohol in a mortar, filtered, and the precipitate washed with methyl alcohol until the filtrate is only yellow. The ochreous residue of nearly pure dihydroanhydro*epi*berberine melts at 165—168°, and was employed in this condition for many of the experiments described in the following pages.* For analysis, the substance was recrystallised from acetone, and two analyses were made with preparations obtained by the two processes described above.

(1) 0·1072 gave 0·2793 CO_2 and 0·0564 H_2O. C=71·1; H=5·8.
0·3967 „ 14·1 c.c. N_2 at 16° and 762 mm. N=4·2.

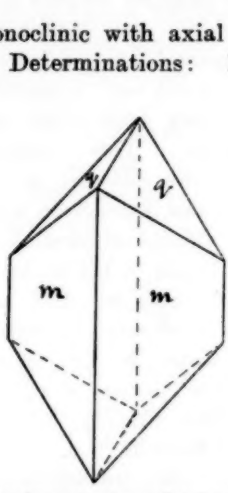
* Owing to the tedious nature of these processes and the labour required in the preparation even of a few grams of dihydroanhydro*epi*berberine, attempts have repeatedly been made to discover conditions under which larger quantities than 2 grams of *iso*cryptopine chloride could be decomposed in one operation, but without success. If, for example, 10 grams of the chloride are heated in a small flask under exactly the conditions observed in the case of the 2 grams, the decomposition appears to proceed in precisely the same way, but the product yields, at the most, traces only of pure dihydroanhydro*epi*berberine. Apparently the time required to decompose 10 grams of *iso*cryptopine chloride is sufficiently long to decompose the product almost entirely.

(2) 0·1179 gave 0·3075 CO_2 and 0·0615 H_2O. C=71·1; H=5·7. $C_{20}H_{19}O_4N$ requires C=71·2; H=5·6; N=4·2 per cent.

*Dihydroanhydro*epi*berberine* melts at 172—174°, and is sparingly soluble in ether or in ethyl or methyl alcohol, even on boiling, and also in cold acetone. It is moderately soluble in boiling acetone, and separates in magnificent iridescent, golden-yellow plates resembling lead iodide, or, if the solution is allowed to cool slowly, in well-defined prisms.

The crystals, obtained from acetone, were measured by Miss M. W. Porter, and the Fedorov complex-symbol was calculated by Mr. T. V. Barker.

The crystals are monoclinic with axial ratios: $a:b:c=1·163:1:0·995$; $\beta=97°15'$. Determinations: 100/001/010. Complex-



Dihydroanhydro*epi*berberine.

symbol, $4o$; 8/44/+4. The forms observed were $m\{110\}$ and $q\{011\}$, with a prismatic habit as shown in the figure. The faces being rounded, the reflections were rather poor. Four crystals were measured and the results obtained are placed in the following table.

Face.	No. of readings.	Azimuth (ϕ). Limits.	Obs	Calc	Polar distance (ρ). Limits	Obs.	Calc
m(110)	11	40°39′—41°13′	*40°56′	—	90° 0′—90° 9′	90°0′	90° 0′
q(011)	4	6 42 — 7 52	*7 7	—	44 56—45 15	*45 5	—

*Dihydroanhydro*epi*berberine* dissolves readily in acetic acid to a deep yellow solution, and the base is not precipitated by dilution with water, but separates on the addition of ammonia as a caseous precipitate which, on warming, becomes crystalline. If a trace of the base, dissolved in a drop of acetic acid, is mixed with sulphuric

acid, there is at first little change, but, on keeping, the solution becomes cherry-red.

Salts of Dihydroanhydroepiberberine.

Hydrochloride, $C_{20}H_{19}O_4N,HCl,3H_2O$.—When dihydroanhydroepiberberine is moistened with hydrochloric acid, it is converted into a yellow powder of the hydrochloride which, whilst very sparingly soluble in cold water, and particularly so in cold dilute hydrochloric acid, dissolves in much boiling water and separates in groups of flat, yellow, prismatic needles. This brilliant orange salt loses its water of crystallisation and becomes brick-red in the steam-oven, but on exposure to the air, it gradually absorbs moisture and becomes yellow again:

0·1319, air-dried salt, lost 0·0157 at 100°. $H_2O=11·9$.

0·1048, dried at 100°, gave 0·2470 CO_2 and 0·0490 H_2O. $C=64·2$; $H=5·2$.

$C_{20}H_{19}O_4N,HCl,3H_2O$ requires $H_2O=12·6$ per cent., and the anhydrous salt requires $C=64·2$; $H=5·3$ per cent.

Hydrobromide.—The addition of boiling dilute potassium bromide to the boiling solution of the hydrochloride gives a brick-red precipitate which consists of groups of striated prismatic needles. For analysis, it was dried at 100°:

0·0810 gave 0·1705 CO_2 and 0·0343 H_2O. $C=57·4$; $H=4·7$.

$C_{20}H_{19}O_4N,HBr$ requires $C=57·4$, $H=4·8$ per cent.

Dihydroanhydroepiberberine Methosulphate, $C_{20}H_{19}O_4N,Me_2SO_4$.—This derivative is best prepared by sealing up the finely divided base (1 gram) with freshly distilled methyl sulphate (1·5 c.c.) in a small tube and shaking vigorously from time to time. There is no evolution of heat on mixing, and combination takes place only very gradually, but is complete in about eight days. The product is triturated with benzene, the yellow mass collected by the aid of the pump, washed with benzene, and recrystallised from methyl alcohol, in which it is sparingly soluble. The prisms which separate on gradual cooling are unfortunately so striated as to be unsuitable for measurement, and the substance also becomes opaque when exposed to the air.

After remaining exposed to the air for eight days, the substance lost only 3·1 per cent. at 100°, and on analysis:

0·1013 gave 0·2115 CO_2 and 0·0531 H_2O. $C=56·9$; $H=5·8$.

$C_{20}H_{19}O_4N,Me_2SO_4$ requires $C=57·0$; $H=5·4$ per cent.

Dihydroanhydroepiberberine methosulphate darkens above 250°

and melts rather sharply at 260° with vigorous decomposition to a black froth. The deep yellow prisms from methyl alcohol become pale yellow on stirring with water, dissolve very sparingly in the cold, but much more freely on boiling, and the solution gelatinises if rapidly cooled. The aqueous solution gives no precipitate with ammonia, and rapidly reduces permanganate even at −5°.

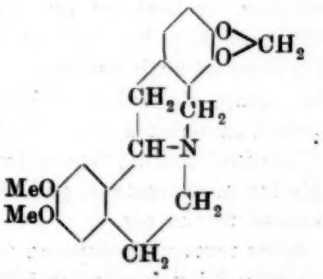
This methosulphate is sparingly soluble in glacial acetic acid, and the addition of sulphuric acid produces, at first, no coloration, then a pale green gradually develops; on keeping, the solution becomes purplish-black, and the addition of a drop of dilute nitric acid changes the colour to intense purple and then to brown. When the finely divided methosulphate is mixed with methyl-alcoholic potassium hydroxide (15 per cent.), it dissolves, but, on boiling, the solution clouds and a pale yellow precipitate separates. This was collected, washed with methyl alcohol, then with water, and dissolved in boiling methyl alcohol, when, on rubbing, minute yellow prisms immediately separated which melted at 108—110°, and consisted of anhydrocryptopine (p. 497).

Dihydroanhydroepiberberine methiodide, $C_{20}H_{19}O_4N,MeI$, is obtained as an immediate, very sparingly soluble, ochreous precipitate when potassium iodide is added to the saturated aqueous solution of the methosulphate, but if the solutions are sufficiently dilute and are mixed boiling, a clear solution may be obtained, from which the iodide separates as a fluffy precipitate consisting of microscopic groups of needles:

0·1135 gave 0·2176 CO_2 and 0·0487 H_2O. C = 52·3; H = 4·7.
$C_{20}H_{19}O_4N,MeI$ requires C = 52·6; H = 4·6 per cent.

This methiodide darkens and softens at about 230°, and then melts and decomposes at about 245° to a deep red syrup.

Tetrahydroanhydroepiberberine,



This substance is most readily obtained by the action of heat on *iso*dihydrocryptopine α-chloride (T., 1916, **109**, 935), but it may also be prepared by the action of heat on the corresponding β-chloride (*loc. cit.*, p. 934). In the case of the α-chloride, the

decomposition is conveniently carried out by heating quantities of not more than 2 grams of the pure dry salt in a test-tube, drawn out to a long capillary, by means of a sulphuric acid bath. At about 270° effervescence sets in, due to the escape of methyl chloride, which may be ignited at the end of the capillary and burns with a green-edged flame.

As soon as the frothing has ceased, the tube is taken out of the bath and left to cool, when the brown syrup will have solidified and the dark product may be purified by crystallisation from boiling alcohol, from which nearly pure tetrahydroanhydro*epi*berberine separates at once in pale brown needles. An alternative method is to convert the crude product into the very sparingly soluble hydrochloride (see below), to purify this by crystallisation from acetic acid, and, after decomposing the colourless salt with dilute alkali, to crystallise the base from much alcohol.

In the case of the β-chloride, decomposition does not proceed so smoothly, owing no doubt to the fact that this chloride fuses with much greater difficulty than the α-chloride. The elimination of methyl chloride is best carried out with quantities of not more than 2 grams in a test-tube heated in a metal-bath under the conditions described in detail in the case of the preparation of dihydroanhydro*epi*berberine from *iso*cryptopine chloride (p. 506). The decomposition of the β-chloride does not begin much below 300°, and should not be pushed to completion, otherwise the product will be very dark coloured and difficult to purify. Purification is best effected by converting the dark resin into the sparingly soluble hydrochloride, crystallising this from acetic acid until it is quite colourless, and then regenerating the base and crystallising this from much alcohol.

*Preparation of Tetrahydroanhydro*epi*berberine by the Reduction of Dihydroanhydro*epi*berberine.*—In the event of the α- or β-chlorides of *iso*dihydrocryptopine not being available, this method is probably the most convenient for the preparation of the tetrahydro-base. Crude dihydroanhydro*epi*berberine (p. 507) is dissolved in hot concentrated hydrochloric acid, the solution diluted with an equal volume of water, and boiled with a large excess of granulated tin for several hours. The product, diluted with much water, is freed from tin by means of hydrogen sulphide in the usual manner, the filtrate from the tin sulphide is concentrated and left for several days, during which the sparingly soluble hydrochloride of tetrahydroanhydro*epi*berberine separates. This is collected, recrystallised, decomposed by alkali, and the base crystallised from much alcohol. Two different specimens gave the following results on analysis:

0·1015 gave 0·2625 CO_2 and 0·0569 H_2O. C = 70·5; H = 6·2.
0·1021 „ 0·2652 CO_2 „ 0·0575 H_2O. C = 70·8; H = 6·3.
0·3965 „ 14·1 c.c. N_2 at 15° and 758 mm. N = 4·2.
$C_{20}H_{21}O_4N$ requires C = 70·8; H = 6·2; N = 4·2 per cent.

Tetrahydroanhydroepiberberine melts at 170—171° and is sparingly soluble in boiling methyl alcohol, but somewhat more readily so in boiling ethyl alcohol, from both of which it separates in colourless needles. It is sparingly soluble in cold acetone, moderately readily so on boiling, and crystallises on slowly cooling in prisms; boiling benzene dissolves the base freely, and, on cooling, it separates in prismatic needles. In purifying specimens of the base, which are highly coloured, acetone is the best solvent. Tetrahydroanhydro*epi*berberine does not exhibit the tendency so marked in the case of tetrahydroanhydroberberine of separating from solvents in stout, well-developed prisms, and unfortunately all attempts to obtain it in a state suitable for measurement have so far been unsuccessful. The solution of a crystal in a drop of acetic acid gives at first no coloration on the addition of sulphuric acid, but gradually a violent tint develops.

Salts of Tetrahydroanhydroepiberberine.

Hydrochloride, $C_{20}H_{21}O_4N,HCl$.—The finely powdered base is immediately converted by moistening with dilute hydrochloric acid into the sparingly soluble hydrochloride, which separates from much boiling water in microscopic bundles of needles like fern fronds:

0·1140 gave 0·2687 CO_2 and 0·0608 H_2O. C = 64·3; H = 5·9.
$C_{20}H_{21}O_4N,HCl$ requires C = 64·0; H = 5·8 per cent.

In its properties, this hydrochloride resembles the sparingly soluble hydrochloride of tetrahydroanhydroberberine, but it appears to be even less readily soluble than the latter in dilute hydrochloric acid, and must be classed as one of the least readily soluble of alkaloid hydrochlorides. When it is heated in a capillary tube, the upper surface in contact with air begins to darken at 195—200°, and becomes orange-red, whilst the remainder is scarcely discoloured; at 285—290°, the whole melts with vigorous effervescence to an orange-red froth. Highly coloured specimens of the hydrochloride are readily obtained colourless by recrystallisation from glacial acetic acid, in which the salt is sparingly soluble and from which it separates in colourless nodules or circular, warty groups, the colouring matter remaining almost entirely in the mother liquor.

The *sulphate* is much more readily soluble than the hydrochloride, and separates either as a jelly or as a voluminous mass of bent and striated needles. When the aqueous solution of this salt is boiled, a very sparingly soluble sulphate gradually separates as a sandy powder.

The *nitrate* separates, on the addition of dilute nitric acid, to the hot solution of the sulphate, as a very sparingly soluble, crystalline powder.

Tetrahydroanhydroepiberberine Methosulphate and its Conversion into Anhydrodihydrocryptopine (A and B).—When tetrahydroanhydro*epi*berberine (3 grams) is mixed with freshly distilled methyl sulphate (4 c.c.), the mixture becomes very warm, liquefies, and then sets to a stiff paste of the methosulphate, which may be freed from the excess of methyl sulphate by washing with benzene and then be crystallised from methyl alcohol. A more convenient method of preparation is to dissolve the base (2 grams) in boiling benzene (10 c.c.), and, after cooling until crystallisation just commences, to add freshly distilled methyl sulphate (3 c.c.).

The clear solution soon begins to deposit the methosulphate as a hard crust, which is collected, washed with benzene, and crystallised from methyl alcohol. An air-dried specimen of the needle-shaped modification of the substance which separates from water (see below) appears to have the formula $C_{20}H_{21}O_4N,Me_2SO_4,3H_2O$:

0·7220, air-dried salt, lost 0·0834 at 100°. $H_2O=11·5$.

0·1201, dried at 100°, gave 0·2486 CO_2 and 0·0635 H_2O. $C=56·5$; $H=5·9$.

$C_{20}H_{21}O_4N,Me_2SO_4,3H_2O$ requires $H_2O=10·4$ per cent., and the anhydrous substance requires $C=56·7$, $H=5·9$ per cent.

Tetrahydroanhydroepiberberine methosulphate melts and decomposes at about 255—260°; it is sparingly soluble in cold methyl alcohol, but readily so on boiling, and separates in large, colourless prisms. It is sparingly soluble in cold water, but dissolves readily on boiling, and the solution either sets to a jelly or deposits the substance in groups of hairs. At some concentrations, the methosulphate is deposited in groups of striated prisms; the liquid then becomes filled with glistening needles, and when warmed the needles dissolve and the prisms remain. It is therefore probably dimorphous.

The hot dilute aqueous solution of the methosulphate gives, on the addition of boiling dilute potassium iodide, a clear solution, from which the iodide separates as a voluminous mass of fine hairs. This substance is *iso*dihydrocryptopine α-iodide, since it melts at

275° and behaves on heating exactly as described in the case of that substance (compare T., 1916, **109**, 937).

Anhydrodihydrocryptopine (A and B).—When tetrahydroanhydro*epi*berberine methosulphate was heated with excess of methyl-alcoholic potassium hydroxide (25 per cent.), it dissolved; the solution then became lilac, and decomposition soon set in, with the separation of potassium sulphate.

After twenty minutes, water was added, the viscid precipitate, which soon became crystalline, collected, left on porous porcelain until dry, and crystallised from much methyl alcohol, in which it was very sparingly soluble. The glistening mass of microscopic prisms which separated on keeping melted at 177—178°, and consisted of anhydrodihydrocryptopine (A), since, on boiling with alcohol for half an hour, evaporating to dryness, and crystallising from methyl alcohol, prisms of anhydrodihydrocryptopine (B) melting at 127° separated (T., 1916, **109**, 941). On analysis, the modification melting at 177—178° gave C = 71·1, H = 6·8, whereas $C_{21}H_{23}O_4N$ requires C = 71·4; H = 6·5 per cent.

The epi*Berberinium Quaternary Salts* (compare p. 499).

These salts are obtained from the salts of dihydroanhydro*epi*berberine or tetrahydroanhydro*epi*berberine by the action of such oxidising agents as bromine, iodine, dilute nitric acid, or mercuric acetate, and of these, the latter reagent, first recommended by Gadamer (*Arch. Pharm.*, 1915, **253**, 274) for such oxidations, gives the best results.

(1) *The Action of Iodine on Tetrahydroanhydro*epi*berberine.*—In studying this process, the pure base (8 grams) was dissolved in boiling alcohol, and then an alcoholic solution of rather less than the calculated quantity of iodine (11 instead of 12 grams) was added in small quantities at a time. The colour disappeared rapidly, especially at first, and a heavy, crystalline precipitate soon commenced to separate. After boiling for thirty minutes, most of the alcohol was distilled off, the residue mixed with very dilute sulphurous acid to remove a trace of iodine, the ochreous precipitate collected, washed, and then boiled for an hour with water and excess of freshly precipitated silver chloride. The product was filtered, the filtrate and washings being concentrated considerably, made slightly alkaline with ammonia, and left in the ice-chest for a couple of days. The brown liquid was filtered from a small quantity of a crystalline base which had separated, the filtrate heated to boiling, and mixed with a large excess of hydrochloric acid. After remaining over night, the crystalline salt was collected

and several times recrystallised from dilute hydrochloric acid, when pure *epi*berberinium chloride was obtained in deep orange needles. For analysis, the salt was dried in the steam-oven at about 90°:

0·1002 gave 0·2265 CO_2 and 0·0476 H_2O. C = 61·7; H = 5·2.
$C_{20}H_{18}O_4NCl,H_2O$ requires C = 61·6; H = 5·2 per cent.

(2) *The Action of Mercuric Acetate on Tetrahydroanhydro*epi*berberine.*—This process was the one employed in the preparation of much of the *epi*berberinium chloride required for this research. Tetrahydroanhydro*epi*berberine (3·5 grams), dissolved in dilute acetic acid (40 c.c. of 25 per cent.), was heated to 50°, and then a solution of mercuric acetate (prepared by dissolving 9 grams of mercuric oxide in hot glacial acetic acid and adding 3 vols. of hot water) was slowly added, when oxidation took place at once and mercurous acetate separated. After heating for a few minutes on the steam-bath, the whole was left in the ice-chest over night, in order that as much mercurous acetate as possible should crystallise out, then filtered by the aid of the pump, and the precipitate washed with ice-water. Hydrogen sulphide was then passed until the liquid smelled strongly of the gas, the whole was then heated on the water-bath, filtered from the mercuric sulphide,* the filtrate made alkaline with ammonia, and left for two days.

A small quantity of unchanged tetrahydroanhydro*epi*berberine which had separated was removed by filtration, the brown filtrate made just acid with hydrochloric acid, concentrated by distillation under diminished pressure, and mixed with a large excess of hydrochloric acid. Almost immediately, *epi*berberinium chloride commenced to separate in orange needles, and this was collected, left in contact with porous porcelain until dry, and washed with a little methyl alcohol, which removed a dark-coloured impurity. Finally, the salt was crystallised from dilute hydrochloric acid, from which it separated in orange needles possessing a striking, satiny lustre. Analysis (1) given below was made with a sample prepared by this process.

(3) *The Action of Mercuric Acetate on Dihydroanhydro*epi*berberine.*—This process, which works well, is conveniently carried out by dissolving dihydroanhydro*epi*berberine (3·5 grams) in dilute

* It is necessary to remove any trace of mercuric salt before precipitating the *epi*berberinium chloride with hydrochloric acid, because otherwise the latter will be contaminated with mercuric double salt. On the other hand, if the solution of the berberinium acetate, as sometimes happens, is very dark coloured, it is a good plan to add excess of mercuric chloride and hydrochloric acid and then to collect the mercuric double salt and decompose this with hot water and hydrogen sulphide. The filtrate is then much less coloured, and yields, on concentration, very pure *epi*berberinium chloride.

acetic acid (30 c.c. of 25 per cent.), adding a solution of mercuric acetate prepared from 4·5 grams of mercuric oxide, and, after remaining over night, heating on the steam-bath for half an hour. The product is worked up exactly in the way explained in detail in the case of the corresponding oxidation of tetrahydroanhydro-*epi*berberine (see above), and yields about 2 grams of pure *epi*berberinium chloride (see analysis 2).

epi*Berberinium chloride*, $C_{20}H_{18}O_4NCl,4H_2O$, separates from water, in which it is comparatively readily soluble, in brilliant orange needles, which when dry have a striking, satiny lustre. It is much less readily soluble in dilute hydrochloric acid than in water, and is best crystallised by adding concentrated hydrochloric acid to the moderately concentrated aqueous solution. It is very sparingly soluble in boiling methyl alcohol, but separates beautifully in striated, orange needles; on the other hand, it dissolves readily in hot glacial acetic acid, and crystallises well from this solvent. When the glistening, orange needles of the chloride are moistened with methyl alcohol, they lose their lustre and become an opaque chrome-yellow powder, a change doubtless due to the loss of the water of crystallisation:

(1) 0·1136, air-dried salt, lost 0·0139 in the steam-bath at about 90°. $H_2O=12·2$.

0·0997 then gave 0·2273 CO_2 and 0·0472 H_2O. $C=62·1$; $H=5·2$.

(2) 0·1073 dried at about 90° gave 0·2437 CO_2 and 0·0491 H_2O. $C=61·9$; $H=5·1$.

$C_{20}H_{18}O_4NCl,4H_2O$ losing $3H_2O=12·17$ per cent.

$C_{20}H_{18}O_4NCl,H_2O$ requires $C=61·6$; $H=5·1$ per cent.

In an experiment in which the salt had been heated in an air-bath at 100—105°, it had darkened somewhat and gave $C=63·7$, $H=4·8$, whereas $C_{20}H_{18}O_4NCl$ requires $C=64·6$, $H=4·8$ per cent. The salt was therefore practically anhydrous.

The *platinichloride* separates as a bright orange-red precipitate when platinic chloride is added to the warm solution of *epi*berberinium chloride in dilute hydrochloric acid:

0·1148 gave 0·1878 CO_2 and 0·0351 H_2O. $C=44·6$; $H=3·4$.

$(C_{20}H_{18}O_4NCl)_2PtCl_4$ requires $C=44·4$; $H=3·3$ per cent.

epi*Berberinium sulphate* is obtained when hot dilute sulphuric acid is added to a concentrated solution of the chloride as a bright yellow salt which crystallises in needles.

The characteristic *picrate* separates as an orange, amorphous precipitate when picric acid is added to a hot dilute solution of the chloride. It melts not very sharply at 222° with decomposition, and is very sparingly soluble even in much boiling water. It is also

very sparingly soluble in boiling alcohol, in which it dissolves to the extent of about 1 gram in a litre, and, on cooling, separates almost completely in flat, microscopic needles melting at 222°.

Action of Sodium Hydroxide on epi*Berberinium Sulphate. Formation of* epi*Berberine* (epi*Berberinal*), *Oxy*epi*berberine, and Dihydroanhydro*epi*berberine* (compare p. 500).

In the introduction to this communication (p. 501), it is explained that berberine (berberinal) is readily obtained by treating berberinium sulphate with concentrated aqueous sodium hydroxide and extracting with ether (Gadamer, *Arch. Pharm.*, 1905, **243**, 34), but this process has not been found so successful in the case of *epi*berberinium sulphate. The best result is obtained when an excess of sodium hydroxide (50 per cent.) is added to a solution of *epi*berberinium sulphate (5 grams) in 500 c.c. of freshly boiled water. The ochreous precipitate which separates is rather sparingly soluble in ether, and the filtered ethereal solution begins almost immediately to deposit needles of oxy*epi*berberine (see below). If, however, the ochreous precipitate is immediately collected in an atmosphere of coal gas, it is almost completely soluble in dilute hydrochloric acid with the formation of *epi*berberinium chloride, and yields, on analysis, numbers agreeing approximately with those required for the formula of *epi*berberine:

0·1090 gave 0·2693 CO_2 and 0·0540 H_2O. C = 67·4; H = 5·4.

$C_{20}H_{19}O_5N$ requires C = 68·0; H = 5·4 per cent.

Oxidation takes place rapidly when the moist substance is left in contact with air, and in the course of a few hours a considerable portion will be insoluble in dilute hydrochloric acid and consist of oxy*epi*berberine.

Completely satisfactory results were obtained in investigating the conversion of *epi*berberinium sulphate into oxy*epi*berberine and dihydroanhydro*epi*berberine by the action of concentrated sodium hydroxide. This decomposition is analogous to that described in the case of the action of sodium hydroxide on berberinium sulphate (compare Gadamer, *loc. cit.*, pp. 35 and 36).

The sulphate (3 grams) is thoroughly mixed with sodium hydroxide (12 c.c. of 20 per cent.), the flask containing the mixture placed in cold water, and the water gradually raised to the boiling point and kept at this temperature for an hour. The product, which is not so dark-coloured as in the case of the corresponding experiment with berberinium sulphate, is diluted with much water, filtered by the aid of the pump, the ochreous powder washed and

then warmed with excess of very dilute hydrochloric acid, when dihydroanhydro*epi*berberine dissolves and a pale ochreous mass with a satiny lustre remains, which consists of nearly pure oxy*epi*berberine. This was thoroughly washed, dried in the steam-oven, dissolved in a little glacial acetic acid, and allowed to remain in a closed test-tube, when deep yellow needles of *oxy*epi*berberine acetate* separated. This was collected, washed with acetic acid, and dried between filter paper:

0·1368 gave 0·3221 CO_2 and 0·0641 H_2O. C = 64·2; H = 5·2.
$C_{20}H_{17}O_5N,C_2H_4O_2$ requires C = 64·2; H = 5·1 per cent.

On exposure to moist air, this acetate gradually becomes opaque, owing to loss of acetic acid, and oxy*epi*berberine remains. The acetate is readily soluble in acetic acid, and if the solution is mixed with two volumes of boiling water, the clear liquid soon becomes filled with needles of oxy*epi*berberine. When the acetate is heated in a capillary tube, it becomes paler at about 110° and melts at 238—240°, the atmosphere of acetic acid having no effect on the melting point, which is that of oxy*epi*berberine. The acetate is quantitatively decomposed at 90—95° into acetic acid and oxy*epi*berberine, as the following experiment shows:

1·2052 lost at 90—95° 0·1736. $C_2H_4O_2$ = 14·4.
$C_{20}H_{17}O_5N,C_2H_4O_2$ requires $C_2H_4O_2$ = 14·6 per cent.

The residue of pure *oxy*epi*berberine* was analysed:

0·1260 gave 0·3145 CO_2 and 0·0557 H_2O. C = 68·1; H = 4·9.
$C_{20}H_{17}O_5N$ requires C = 68·3; H = 4·8 per cent.

*Oxy*epi*berberine* gradually darkens above 210° and melts approximately at 240—241° to a dark brown syrup. It is very sparingly soluble even in boiling alcohol, and separates in well-developed rhombic plates, the angle of the rhomb being 66°; in polarised light, diagonal extinction.

*Dihydroanhydro*epi*berberine.*—The hot dilute hydrochloric acid filtrate which had been separated from the oxy*epi*berberine, as explained above, was mixed with more hydrochloric acid and left in the ice-chest, when it deposited a voluminous mass of slender, orange needles. This salt was collected, recrystallised from dilute hydrochloric acid, dissolved in hot water, and rendered alkaline with ammonia, when a milky liquid resulted which was extracted with much ether. After rapidly drying over potassium carbonate and concentrating, striated, lemon-yellow prisms separated, on keeping, which melted at 172°, and consisted of dihydroanhydro*epi*berberine (Found: C = 71·0; H = 5·7. $C_{20}H_{19}O_4N$ requires C = 71·2; H = 5·6 per cent. Compare p. 508).

iso*Oxy*epi*berberine* (compare p. 501).

The conversion of oxyberberine into *iso*oxyberberine takes place gradually when the former is heated with dilute hydrochloric acid at 130° (Bland, Perkin, and Robinson, T., 1912, **101**, 264), but recent experiments have shown that the change occurs much more readily and completely when a temperature of 150—160° is employed.

In attempting to convert oxy*epi*berberine into *iso*oxy*epi*berberine, the conditions originally employed in the case of the corresponding conversion of oxyberberine into *iso*oxyberberine were adhered to, and the temperature was kept at 130° for five hours, but, on working up the contents of the sealed tube, practically the whole of the oxy*epi*berberine was recovered unchanged. Some slight action had taken place, because, on opening the tube, the liquid on the sides of the walls became coloured purple by the action of the air. When, however, the experiment was repeated at 150—160° for six hours, complete transformation had taken place. The contents of the tube were filtered by the aid of the pump, the residue washed and boiled out with glacial acetic acid, in which *iso*oxy*epi*berberine is very sparingly soluble. The ochreous mass was then dissolved in boiling pyridine and filtered, when the substance separated as a voluminous mass of microscopic needles. It was collected, washed with hot methyl alcohol, and dried at 100°:

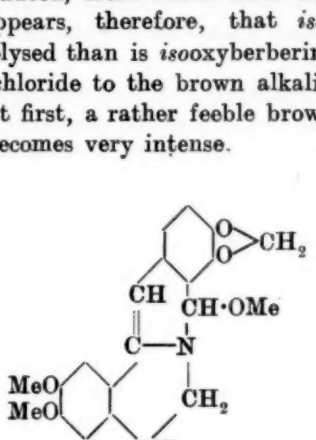
0·0984 gave 0·2473 CO_2 and 0·0448 H_2O. C = 68·5; H = 5·0.

$C_{20}H_{17}O_5N$ requires C = 68·4; H = 4·8 per cent.

*iso*Oxy*epi*berberine scarcely darkens at 270°, but gradually blackens at 300° without melting. It is almost insoluble in the usual solvents, including boiling glacial acetic acid, in which the isomeric *iso*oxyberberine is comparatively readily soluble. A trace of the substance, rubbed on the sides of a test-tube, is coloured violet by sulphuric acid and dissolves to a pale brown solution; in the case of a similar experiment with nitric acid, the substance is coloured violet and dissolves to a deep bluish-violet solution, which becomes permanganate colour on the addition of water. When the suspension of the substance in alcohol is mixed with ferric chloride and warmed, a green colour develops. A very delicate reaction is obtained by dissolving a trace of *iso*oxy*epi*berberine in boiling glacial acetic acid, cooling, and adding an equal volume of sulphuric acid. The addition of a drop of dilute nitric acid to the pale yellow solution produces a most intense violet coloration, and this, on dilution with water, becomes magenta. *iso*Oxy-

berberine is insoluble in aqueous or alcoholic alkali even on boiling (compare *loc. cit.*, p. 264), but *iso*oxy*epi*berberine is coloured deep brown by methyl-alcoholic potassium hydroxide, and dissolves, on warming, to a brown solution, from which a crystalline substance—probably a potassium salt—separates. On the addition of water, a brown solution is produced, from which acids liberate a flocculent precipitate. It appears, therefore, that *iso*oxy*epi*berberine is more readily hydrolysed than is *iso*oxyberberine. The addition of benzenediazonium chloride to the brown alkaline solution in aqueous alcohol gives, at first, a rather feeble brownish-red colour, but, on warming, this becomes very intense.

O-*Methyl*epi*berberine*,



,

O-*Ethyl*epi*berberine, and Anhydro*epi*berberine-acetone.*

O-Methyl*epi*berberine is readily prepared from *epi*berberinium chloride or sulphate, either by the action of methyl-alcoholic potassium hydroxide or of sodium methoxide, and of these the latter is to be preferred.

(1) *epi*Berberinium chloride loses its brilliant colour when it is mixed with methyl-alcoholic potassium hydroxide (10 per cent.), and a pale drab, crystalline precipitate separates, especially on warming gently.

This was collected, washed with methyl alcohol, then with water, and again with methyl alcohol, and found to consist of practically pure *O*-methyl*epi*berberine. For the analysis given below, a little of it was rapidly recrystallised from methylal, from which it separated in yellowish-brown prisms.

(2) The best method for preparing the *O*-methyl derivative is the following: *epi*Berberinium chloride (2 grams), suspended in methyl alcohol, is heated on the steam-bath, sodium (1 gram) dissolved in methyl alcohol added, and the whole rapidly filtered. Crystallisation begins at once, and pure *O*-methyl*epi*berberine separates in a most beautiful manner in glistening, old-gold prisms. After remaining until cold, these were collected and washed with methyl alcohol.

The following analyses were made with specimens obtained from each of the above methods of preparation:

(1) 0·1088 gave 0·2723 CO_2 and 0·0570 H_2O. C = 68·3; H = 5·8.
(2) 0·1111 „ 0·2798 CO_2 „ 0·0582 H_2O. C = 68·7; H = 5·8.

$C_{21}H_{21}O_5N$ requires C = 68·6; H = 5·7 per cent.

O-*Methyl*epi*berberine* melts at about 150—152° with decomposition to a black froth. Attempts to recrystallise it with the object more particularly of obtaining crystals suitable for measurement and comparison with *O*-methylberberine were unsuccessful. This is mainly due to the fact that the substance undergoes decomposition on boiling with such solvents as methylal or methyl alcohol, and a substance separates which melts at about 230—240°, and was readily identified as oxy*epi*berberine (p. 518). *O*-Methyl*epi*berberine is immediately converted by dilute hydrochloric acid into a deep orange-red salt which crystallises from dilute hydrochloric acid in brilliant orange needles, gives no precipitate when ammonia is added to its aqueous solution, and consists of *epi*berberinium chloride.

O-*Ethyl*epi*berberine*, $C_{20}H_{18}(OEt)O_4N$, is prepared in a similar manner to the *O*-methyl derivative by boiling *epi*berberinium chloride with alcohol, adding excess of sodium ethoxide, and immediately filtering by the aid of the pump, when, on keeping in the ice-chest, circular, crystalline masses soon begin to form. After twenty-four hours, these were collected, washed first with alcohol, then with water, and dried at 80°:

0·1109 gave 0·2808 CO_2 and 0·0598 H_2O. C = 69·1; H = 6·0.

$C_{22}H_{23}O_5N$ requires C = 69·3; H = 6·0 per cent.

O-*Ethyl*epi*berberine* melts and decomposes at about 135—136°, and is sparingly soluble in boiling alcohol, from which it separates in groups of striated needles. It is apparently not so readily converted into oxy*epi*berberine as the corresponding *O*-methyl derivative. It dissolves readily in boiling dilute hydrochloric acid, and *epi*berberinium chloride separates on cooling.

*Anhydro*epi*berberine-acetone*, $C_{20}H_{18}(CH_2{\cdot}COMe)O_4N$. — *O*-Methyl*epi*berberine dissolves readily in boiling acetone, and, if the solution is concentrated and set aside, a crust of yellow prisms of anhydro*epi*berberine-acetone gradually separates, but this substance does not crystallise with the same facility nor is it so highly characteristic as anhydroberberine-acetone. After recrystallisation from acetone, the substance melted not very sharply at about 162° and gave the following results on analysis:

0·1107 gave 0·2846 CO_2 and 0·0586 H_2O. C = 70·1; H = 5·9.

$C_{23}H_{23}O_5N$ requires C = 70·2; H = 5·9 per cent.

The author wishes to state that the cost of the material required for this investigation was partly defrayed by a grant from the Royal Society Research Fund.

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XLIII.—*Water-in-oil Emulsions.*

By ALFRED ULRICH MAX SCHLAEPFER.

WITH a system consisting of two liquid phases, *A* and *B*, it is theoretically possible to obtain two classes of emulsions, namely, *A*-in-*B* emulsions, in which *A* is the disperse phase and *B* the medium, and *B*-in-*A* emulsions, in which *B* is the interior and *A* the exterior phase (compare Wo. Ostwald, *Kolloid Zeitsch.*, 1910, **6**, 103).

At first, the power of producing emulsions was exclusively attributed to substances which, when dissolved in one of the liquid phases, reduce the tension on their interface, thus facilitating the dispersion of one of them in the other.

Pickering (T., 1907, **91**, 2001) was the first to prove that it is possible to obtain emulsions of hydrocarbon oils in water by means of solid emulsifiers, such as precipitates of basic copper sulphate, basic iron sulphate, etc., which are insoluble in either liquid and are moistened more by water than by the oil. He showed that the finely divided particles of the emulsifier form a coat over the oil droplets, preventing their coalescence. The action of the particles of hydrophile colloids, such as soap, etc., which had long been known as excellent emulsifiers, he considered to be similar to that of the grains of basic copper sulphate.

Pickering showed also that the type of an emulsion is largely independent of the proportions in which the two phases are present when he prepared emulsions of kerosene (disperse phase) in dilute soap solution (medium) containing up to 99 per cent. of kerosene in a 1 per cent. soap solution. Such emulsions, in which the disperse phase is greatly in excess over the medium, show an extremely high viscosity. Pickering did not consider the possibility of making emulsions of water in oil.

As Bancroft (*J. Physical Chem.*, 1912, **16**, 475) pointed out in his discussion of Pickering's results, it is to be expected as their

corollary that insoluble particles, which are more easily moistened by oil than by water, will have a tendency to facilitate the emulsification of water in oil. In other words, if the solid particles of the emulsifiers have a lower surface tension with the phase *A* than with the phase *B*, it is to be expected that an emulsion will be formed with *A* as medium and *B* as disperse phase, and vice versa.

Newman (*J. Physical Chem.*, 1914, **18**, 34) found that soaps of certain alkaline earths, especially those containing magnesium, were excellent emulsifiers for emulsions of water in benzene. He showed also that mixed paints which contain a certain amount of water are to be considered as emulsions of the water-in-oil type. He drew the conclusion that in the latter case the emulsifying properties are to be ascribed to rosin and not to the pigment.

The experiments described below are concerned with the preparation of water-in-oil emulsions with the aid of a finely divided solid insoluble in both liquids, which is more easily wetted by the oil than by the water phase.

Experimental.

Materials Used.

Kerosene.—A water-white kerosene fraction (D^{15} 0·785) was redistilled over sodium. Distillation by Redwood's method gave the following result:

Distillate per cent.	0	10	20	30	40	50	60	70	80	90	95
Boiling point	156°	158°	160°	161°	166°	170°	174°	176°	182°	192°	208°

Carbon.—Best American carbon black (gas black, soot) was extracted for two days with hot benzene.

The distilled water was obtained from a tinned copper still.

The following experiments were carried out with these materials.

Experiment 1.—Thirty c.c. of water, 70 c.c. of kerosene, and 1 gram of carbon were shaken together in a flask. In this way, an emulsion was obtained which contained water as the disperse phase. This could easily be shown on a watch-glass by the fact that the emulsion mixed freely with kerosene, but not with water. Under a microscope, it was found that the droplets of water were covered with a dark brown skin of adsorbed particles of carbon. Those particles which were not adsorbed formed aggregates in the kerosene phase. The emulsion was liquid. After remaining for one day, it separated into pure kerosene, floating on the top, and a viscid emulsion which was still of the water-in-kerosene type and was stable for several weeks.

Experiment 2.—Seventy c.c. of water, 30 c.c. of kerosene, and

1 gram of carbon were shaken in a flask. In this, as in the other experiments here described, it was immaterial whether the carbon was added first to the water or to the oil or to both when mixed. The emulsion mixed freely with kerosene but not with water, and was therefore again of the water-in-oil type. It was so viscid that it did not flow out of a reversed test-tube. It kept for more than a week without altering.

To show the influence of the quantitative proportions of the two phases more clearly, experiments were made in order to determine the time of flow of the emulsions from a 5 c.c. pipette. For the same pipette (all experiments were carried out at about 18°), water required on an average 3·3 seconds and the kerosene 3·5 seconds. The results of these experiments are shown in the table on p. 525.

In this case, the emulsions were prepared in the manner recommended by Pickering, by alternately filling and emptying a garden syringe. The number of strokes, which is a crude criterion of the amount of mixing, has a certain influence on the viscosity of the mixture. The table clearly shows the enormous increase of viscosity which is produced by an increasing proportion of the inner phase.

In experiments 7 and 8, it was not possible to get all the water into the emulsion. It is worth special notice that neither in these nor in any other similar experiments was it ever possible to obtain an emulsion of kerosene in water with the aid of carbon. When the amount of water was too large to be carried by the kerosene, an emulsion with less water was formed, together with an unaltered residuum of water. Since the size of droplets occurring together changed within a large range, especially in the emulsions containing a large amount of water, it does not seem justifiable to make any speculations on the fact that the limit of stability under the described conditions was about 70 per cent. water-content (compare Wo. Ostwald, *loc. cit.*). More water could be added by stirring, but in consequence of the considerable tension on the interface of the two liquids, the droplets stirred in were large. It might, of course, be possible to obtain emulsions of higher water-concentration with carbon black if a fourth compound were added to lower the surface tension between the two liquid phases.

Similar emulsions could be made in an analogous way, using turpentine, benzene, toluene, etc., instead of kerosene.

It may be stated that carron oil, the well-known liniment for burns which is prepared with lime-water and linseed or rape oil, is an emulsion of the water-in-oil type, whilst embrocations are well known to be of the oil-in-water type.

Carron oil mixes freely with organic solvents, but not with water

No of Expt.	Quantities used.			Time required for emulsion to flow out of 5 c.c. pipette* (Means of 6 experiments each)			Amount of kerosene in c.c. floating on top of 100 c.c. of emulsion after twenty-four hours.	Percentage of water in residual emulsion after twenty-four hours.	Remarks.
	Kerosene, c.c.	Water, c.c.	Carbon, grams.	After 160 strokes with syringe.	After 320 strokes with syringe.	After 480 strokes with syringe.			
3	240	60	1·5	4·4	4·7	5·3	48	38·5	Diameter of droplets 0·001—0·02 mm.
4	180	120	1·5	7·4	7·8	—	not measured	—	—
5	120	180	1·5	—	26	44	11	67·5	—
6	90	210	1·5	Did not flow out of pipette or from reversed test-tube.			none	—	Diameter of droplets 0·001—0·1 mm.
7	60	240	1·5	Emulsified part did not flow out of pipette or a reversed test-tube.					It was not possible to emulsify all the water in the experiments. An emulsion of water in kerosene was obtained besides pure water. No emulsion of kerosene in water could be obtained.
8	60	240	3·0						

* As marks, the 5 c.c. mark on the upper tube and the beginning of the lower tube at the bottom of the bulb were taken.

without shaking, and easily dissolves oil colours, but not dyes soluble in water.

Summary.

(1) It is possible to make emulsions of water as disperse phase in organic solvents with the aid of finely divided carbon as emulsifier.

(2) The carbon particles, without leaving the oil phase, form a skin over the water droplets, preventing their coalescence.

(3) The order in which the ingredients are added does not make any difference to the final product.

(4) The emulsions obtained in this way are the more viscous the more water they contain.

(5) Carron oil is a water-in-oil emulsion.

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XLIV.—*The Relationship between the Optical Rotatory Powers and the Relative Configurations of Optically Active Compounds. The Influence of certain Inorganic Haloids on the Optical Rotatory Powers of α-Hydroxy-acids, α-Amino-acids, and their Derivatives.*

By GEORGE WILLIAM CLOUGH.

The Walden Inversion.

THE discovery of the phenomenon known as the Walden inversion was made in connexion with transformations of certain derivatives of succinic acid, and it therefore seemed possible that the change of configuration was due either to the presence of an atom of hydrogen attached to the asymmetric carbon atom or to the fact that the optically active compounds in question were carboxylic acids. Although the configurative change may be due to one or both of these causes in certain cases, it has been shown that a Walden inversion can be effected in a compound containing a tertiary asymmetric carbon atom (McKenzie and Clough, T., 1910, **97**, 1016), and also in compounds which do not contain a carboxyl

group. In his studies on this phenomenon, Fischer observed that the action of a reagent on an ester frequently yielded a compound of the enantiomorphous configuration to that of the compound produced by the same reagent on the corresponding acid, and in such examples he assumed that the action on the ester was not accompanied by change of configuration. That an inversion is possible in the case of an ester has been shown by the fact that phosphorus pentachloride and thionyl chloride yield chloro-esters of opposite signs when they react with the same optically active ethyl α-phenyl-lactate (McKenzie and Clough, T., 1910, **97**, 2564). Further, it is not necessary that the optically active compound should contain either a carboxyl or carbalkyloxy-group, for it has been found possible to effect the interconversion of the optically active phenylmethylcarbinols (T., 1913, **103**, 687).

Several attempts have been made to decide in which reactions an inversion occurs by employing certain assumptions regarding the mechanism of the reactions in question (Armstrong, T., 1896, **69**, 1399; Gadamer, *Chem. Zeit.*, 1910, **34**, 1004; 1912, **36**, 1327; Biilmann, *Annalen*, 1911, **388**, 338). It has been shown that Biilmann's hypothesis cannot be applied to all the examples which have been investigated (McKenzie and Clough, *loc. cit.*), and, moreover, Senter and Drew's experiments (T., 1916, **109**, 1091) concerning the influence of the solvent on the rotatory sign of the phenylaminoacetic acids produced by the action of ammonia on the active phenylchloroacetic acids emphasise the difficulty of drawing conclusions regarding the specific action of a reagent from considerations of the probable mechanism of the reactions. It may still be said that "there does not exist at the present time any criterion whereby the relation between the configuration of an optically active compound and that of a derivative from it can be decisively ascertained" (Frankland, T., 1913, **103**, 738).

Accordingly, it seemed desirable that the problem should be investigated by an entirely different method. The present author has therefore made experiments with the object of ascertaining whether the measurements of the rotatory powers of similarly constituted compounds would reveal regularities between the rotatory values and the relative configurations of the active compounds. In such an investigation, it is necessary to consider the influence of the conditions (temperature, solvent, and concentration) on the rotatory powers of each compound, and also to study the relative effects of substituents introduced into the groups attached to the asymmetric carbon atom. It would, indeed, be impossible to draw a sharp distinction between these two methods of procedure if the assumption is made that some solvents form labile compounds

with the active solute (compare Walden, *Ber.*, 1905, **38**, 408). When it is also recalled that the work of Pickard and Kenyon has brought to light surprising regularities when the rotations of derivatives from a given compound are measured for light of different wave-lengths, it is evident that an entirely satisfactory comparison of the optical rotatory powers of two parent compounds can be made only when the rotatory powers of the compounds and their derivatives have been measured under many varying conditions. Fortunately, the labours of Frankland, Guye, Purdie, Patterson, Walden, and others have resulted in the accumulation of much data available for a comparison of the rotatory powers of the common optically active aliphatic α-hydroxy-acids, whilst the publications of Fischer contain rotation constants for the majority of the active α-amino-acids. The measurements made by the author are by no means as comprehensive as could be wished, but it appears desirable to place on record the results which have been obtained for several α-hydroxy- and α-amino-acids, and to discuss these from the above point of view, especially as conclusions have been drawn concerning the relative configurations of compounds of the sugar series from a consideration of their rotatory powers (Hudson, *J. Amer. Chem. Soc.*, 1917, **39**, 462). In the present paper, attention is directed particularly to regularities observed in the effect of temperature and of certain inorganic haloids on the optical rotatory powers of some α-hydroxy- and α-amino-acids and esters in aqueous or methyl-alcoholic solution.

α-Hydroxy-acids and their Derivatives.

In previous communications (T., 1914, **105**, 49; 1915, **107**, 96. 1509), it has been established that the optical rotatory powers of configuratively similar hydroxy-derivatives of succinic acid containing a carboxyl or carbalkyloxy-group are influenced in the same sense by the presence of the haloids of the alkali or alkaline earth metals in aqueous solutions. These salts diminish considerably the numerical values for the specific rotatory powers and frequently reverse the sign of rotation. With the view of ascertaining whether other hydroxy-acids and esters are, in this respect, similar to malic and tartaric acids, the author has examined the rotatory powers of *l*-lactic acid, methyl *l*-lactate, and *d*-glyceric acid in aqueous solution and in aqueous solutions of certain neutral salts. It is well known that *l*-lactic acid, which is lævorotatory in aqueous solution, yields dextrorotatory salts and esters. The lævorotatory power of this acid in aqueous solution diminishes with rise of temperature, and is ultimately reversed. The influence of temperature on the

optical rotatory power of *l*-lactic acid in aqueous solution is thus similar to that on methyl *l*-lactate in the homogeneous condition, for Patterson and Forsyth observed that rise of temperature increases the dextrorotatory power of this ester (T., 1913, **103**, 2263). The presence of sodium or barium haloids increases the lævorotatory power of *l*-lactic acid (table I), and similarly the dextrorotatory power of methyl *l*-lactate in aqueous solution is diminished or reversed by the salts employed (table II). The rotatory values being usually small, the measurements recorded are for mercury-green light ($\lambda = 5461$).

TABLE I.

The Influence of Sodium Chloride, Sodium Bromide, and Barium Bromide on the Optical Rotatory Power of l*-Lactic Acid* in Aqueous Solution.*

Salt.	Grams of salt added to 25 c.c. of solution.	p.	d^{15}.	$\alpha_{gr.}^{15}$ ($l=4$).	$[\alpha]_{gr.}^{15}$.
None	—	10·73	1·027	− 0·95°	− 2·2°
Sodium chloride	5·85	8·71	1·162	− 3·08	− 7·6
Sodium bromide	10·30	7·65	1·293	− 3·16	− 8·0
Barium bromide	14·80	6·79	1·485	− 7·10	− 17·7

* This specimen contained 8 per cent. of *d*-lactic acid.

TABLE II.

The Influence of Inorganic Salts on the Optical Rotatory Power of Methyl l*-Lactate* in Aqueous Solution.*

Solvent.	p.	d^{20}.	$\alpha_{gr.}^{20}$ ($l=2$).	$[\alpha]_{gr.}^{20}$.
None	100	1·093	+ 18·34°	+ 8·4°
Water	10·0	1·012	+ 0·29	+ 1·4
Aqueous sodium chloride (N)	10·0	1·050	+ 0·11	+ 0·5
,, ,, ,, (4-N)	10·37	1·150	− 0·50	− 2·1
,, sodium bromide (N)	10·0	1·080	+ 0·10	+ 0·5
,, potassium chloride (N)	10·0	1·054	+ 0·10	+ 0·5
,, ammonium chloride (N)	10·0	1·027	+ 0·19	+ 0·9
,, calcium chloride (N)	10·0	1·054	− 0·22	− 1·0
,, barium chloride (N)	10·0	1·094	− 0·28	− 1·3
,, barium bromide (4-N)	9·81	1·456	− 2·60	− 9·1

* This specimen contained 5 per cent. of methyl *d*-lactate.

Notwithstanding the fact that the influence of water on the rotatory power of methyl *l*-lactate is opposite in sense to that of this solvent on the esters of *d*-malic acid or *d*-tartaric acid, it is obvious that the changes of rotation caused by the inorganic haloids are the same in character for *l*-lactic acid and methyl *l*-lactate as

for the configuratively similar compounds *d*-tartaric acid and methyl *d*-tartrate. On the other hand, the changes observed in the case of *d*-glyceric acid are opposite in character to those for *l*-lactic acid. Frankland and Frew have shown that *d*-glyceric acid is dextrorotatory in aqueous solution at the ordinary temperature, but that the specific rotation $[\alpha]_D$ becomes zero in dilute solution (T., 1891, **59**, 96); moreover, this acid yields lævorotatory salts and esters (T., 1893, **63**, 297, 511, 1410). The author finds that *d*-glyceric acid in aqueous solution becomes lævorotatory on raising the temperature, and that the addition of certain inorganic haloids increases the rotation of the acid (table III).

TABLE III.

The Influence of Sodium Chloride and Barium Chloride on the Optical Rotatory Power of d-*Glyceric Acid in Aqueous Solution.*

Salt.	Grams of salt added to 25 c.c. of solution.	*p*.	$d^{20°}$.	$\alpha^{20}_{gr.}(l=2)$.	$[\alpha]^{20}_{gr.}$.
None	—	2·40	1·01	± 0·00°	± 0·0°
Sodium chloride	5·85	1·84	1·17	+ 0·21	+ 4·9
Barium chloride	5·20	1·90	1·22	+ 0·32	+ 6·9

The earlier experiments of Stubbs (T., 1911, **99**, 2265), Patterson and Anderson (T., 1912, **101**, 1833), and the present author concerning the influence of neutral salts on the optical rotatory powers of certain compounds in solution were made with aqueous solutions. Patterson and Anderson, however, found that the dissolution of certain salts in homogeneous ethyl tartrate depressed the rotation of this ester. Walden observed that ethyl tartrate ($\alpha^{1·5}_D$ + 6·1°, $l=1$), after saturation with hydrogen bromide, gave $\alpha^{1·5}_D$ − 7·0° ($l=1$) (*Ber.*, 1905, **38**, 407). It has now been found that the dissolution of about 5 per cent. of calcium chloride in methyl *l*-lactate depresses the rotation from $\alpha^{15}_{gr.}$ + 8·55° to $\alpha^{15}_{gr.}$ + 5·5° ($l=1$). In this connexion, it should be stated that a solution of calcium chloride in this ester readily deposits a crystalline *compound* of the formula $CaCl_2,4C_4H_8O_3$ (Found: Cl = 13·4. Calc.: Cl = 13·5 per cent.). A similar compound of calcium chloride with ethyl lactate has been described by Strecker (*Annalen*, 1854, **91**, 355). Measurements of the rotatory powers of several compounds dissolved in methyl alcohol and in methyl alcohol containing sodium bromide show that the effect of this salt is even greater in methyl alcohol than in water (table IV).

TABLE IV.

The Influence of Sodium Bromide on the Optical Rotatory Powers of l-*Malic Acid,* d-*Tartaric Acid, Methyl* l-*Lactate, Methyl* l-*Malate, and Methyl* d-*Tartrate in Methyl-alcoholic Solution.*

Compound.	$[\alpha]^{15}_{gr.}$ (in methyl alcohol, $c=10$).	$[\alpha]^{15}_{gr.}$ (in methyl-alcoholic sodium bromide, N, $c=10$).
l-Malic acid	− 5·9°	+ 21·8°
d-Tartaric acid	+ 2·6	− 9·0
Methyl *l*-lactate	+ 5·4	− 5·8
Methyl *l*-malate	− 9·4	+ 9·1
Methyl *d*-tartrate	+ 2·7	− 12·6

It is of interest to note that sodium bromide exerts a distinct influence on the rotatory powers of the methyl and ethyl esters of *d*-diacetoxysuccinic acid in methyl-alcoholic solution, but the effect observed is opposite in character to that of the same salt on the corresponding esters of *d*-tartaric acid. Methyl *d*-diacetoxysuccinate gave $[\alpha]^{15}_{gr.}$ −18·3° in methyl alcohol ($c=4$), whilst in *N*-methyl-alcoholic sodium bromide the value was $[\alpha]^{15}_{gr.}$ −12·2° ($c=4$); similarly, for ethyl *d*-diacetoxysuccinate the values obtained were $[\alpha]^{13}_{gr.}$ +3·6° ($c=5$) and $[\alpha]^{13}_{gr.}$ +7·6° ($c=5$) respectively. It thus appears that the specific effect of salts on the optical rotatory powers of hydroxy-acids and esters is due to the presence of alkylic hydroxyl groups in these compounds.

Now, Freudenberg (*Ber.*, 1914, **47**, 2037) has shown that the four hydroxy-acids, *l*-lactic acid, *l*-glyceric acid, *d*-malic acid, and *d*-tartaric acid, all possess the same relative configurations, that is to say, the hydrogen atoms, the hydroxyl and carboxyl groups attached to the asymmetric carbon atoms have a similar spatial disposition in the molecules of these compounds. These relationships have been proved by transformations which do not involve replacements of groups directly attached to the asymmetric carbon atom, and inasmuch as no example is known in which such a change produces inversion, it is justifiable to assume that no configurative change occurs in these reactions. When the rotatory powers of these four acids and of their derivatives are compared, the regularities observed are extremely striking and significant, especially when it is remembered that malic and tartaric acids are dibasic (and may thus be regarded also as β-hydroxy-acids), and that tartaric acid contains two adjacent asymmetric carbon atoms. It has been shown by the author that the influence of temperature on the rotatory powers of these related acids * in aqueous solution

* *l*-Malic acid was examined, but the discussion is simplified by reference to *d*-malic acid.

is similar in character for the four compounds, the dextrorotation being increased (or the lævorotation diminished) in each case. The rotations are also increased by dilution, and the molecular rotations of the sodium or potassium salts in aqueous solution are in each case higher (that is, more positive) than those of the free acids in aqueous solution. Further, the presence of inorganic haloids influences the rotatory powers of the acids in aqueous solution in the same sense.

Similar regularities are observed on examination of the rotatory values of the esters of these acids. Thus the temperature–rotation curves for methyl *l*-lactate (Patterson and Forsyth, *loc. cit.*), methyl *l*-glycerate (Frankland and McGregor, T., 1894, **65**, 768), methyl *d*-malate (Clough, T., 1915, **107**, 103), and methyl *d*-tartrate (Pictet, *Jahresber.*, 1882, 855) are all similar in character. The molecular rotations of the esters, which are higher than those of the parent acids (calculated, where possible, by extrapolation), increase, in the case of the lower members of the homologous series, with increase of molecular weight. The influence of a given solvent* on the rotations of esters of the configuratively related acids, *d*-tartaric acid, *d*-malic acid, and *l*-lactic acid, is in general the same in character, the elevating effect of aromatic nitro-compounds and the depressing effect of aliphatic halogen compounds being particularly striking. It must be stated that there are a few important exceptions to this rule. The regularities observed when inorganic salts are dissolved in solutions of esters of the acids in question are well illustrated by table IV. It therefore appears that, in general, changes of the same character are brought about in the optical rotatory powers of the similarly con-

TABLE V.

The Influence of Substituents on the Molecular Rotations $[M]_D$ *of* l-*Lactic Acid,* l-*Glyceric Acid,* d-*Malic Acid, and* d-*Tartaric Acid.*

	Y = H.	Y = Me.	Y = Et.
l-$CH_3{\cdot}CH(OH){\cdot}CO_2Y$	− 2° (H_2O, $c = 5$)	+ 8·6°	+ 12·2°
l-$CH_2(OH){\cdot}CH(OH){\cdot}CO_2Y$	− 2·3 (H_2O, $c = 20$)	+ 5·8	+ 12·3
d-$CO_2Y{\cdot}CH_2{\cdot}CH(OH){\cdot}CO_2Y$ ...	− 6·3*	+ 11·1	+ 19·8
d-$CO_2Y{\cdot}(CH{\cdot}OH)_2{\cdot}CO_2Y$	− 4·2*	+ 3·8	+ 15·9

	X=Ac, Y=Et.	X=Bz, Y=Me.	X=Me, Y=Me.
l-$CH_3{\cdot}CH(OX){\cdot}CO_2Y$	+ 79·7°	− 59·0°	+ 112·7°
l-$CH_2(OX){\cdot}CH(OX){\cdot}CO_2Y$	+ 35·6	− 89·2	+ 103·5
d-$CO_2Y{\cdot}CH_2{\cdot}CH(OX){\cdot}CO_2Y$	+ 52·3	+ 11·4	+ 92·4
d-$CO_2Y{\cdot}(CH{\cdot}OX)_2{\cdot}CO_2Y$	+ 10·0	− 123·6	+ 180·0

* By extrapolation, Winther, *Zeitsch. physikal. Chem.*, 1902, **41**, 181; or other references, see Frankland and Gebhard, T., 1905, **87**, 865.

stituted optically active α-hydroxy-acids possessing the same relative configurations by similar alterations of temperature, by dissolution in a given solvent, or by the addition of a given optically inactive substance to solutions of the active compounds. Further, it is evident from table V that the introduction of a given radicle into the molecules of the configuratively similar hydroxy-acids in question usually produces alterations of the same character in the rotatory powers.

It should now be possible to determine the relative configurations of similar α-hydroxy-acids with reference to *d*-tartaric acid, but unfortunately in no case are the available data so comprehensive as in the above examples. A comparison of the values for derivatives from *l*-α-hydroxybutyric acid (Guye and Jordan, *Compt. rend.*, 1895, **120**, 1274) with those in table V indicates that *l*-α-hydroxybutyric acid possesses a configuration similar to that of *l*-tartaric acid.

	X=H, Y=NH_4.	X=H, Y=Et.	X=H, Y=*iso*Bu.	X=Ac, Y=*iso*Bu.	X=Bz, Y=*iso*Bu.
l-C_2H_5·CH(OX)·CO_2Y	$[M]_D$ −16·8° (H_2O)	−2·5°	−12·3°	−62·0°	+3·2°

The author has examined the influence of sodium chloride (or bromide) on *d*-β-phenyl-lactic acid and its methyl ester (table VI) with results which, taken in conjunction with those in table IV, show that this acid is related configuratively to *d*-tartaric acid.

TABLE VI.

The Influence of Sodium Haloids on the Optical Rotatory Powers of d-β-*Phenyl-lactic Acid and Methyl* d-β-*Phenyl-lactate in Solution.*

Compound.	Solvent.	c.	t.	$a^t_{gr.}$ (l=2).	$[a]^t_{gr.}$.
d-β-Phenyl-lactic acid ...	Water	2·505	20°	+ 1·28°	+ 25·5°
„ „ „ ...	Aqueous sodium chloride (4*N*)	0·665	20	+ 0·18	+ 13·5
„ „ „ ...	Methyl alcohol	10·0	20	+ 4·20	+ 21·0
„ „ „ ...	Methyl-alcoholic sodium bromide (*N*).....	10·0	20	− 0·41	− 2·0
Methyl *d*-β-phenyl-lactate	Methyl alcohol...	10·0	18	− 0·90	− 4·5
„ „ „	Methyl-alcoholic sodium bromide (*N*)	10·0	18	− 4·46	− 22·3

The values for *l*-α-hydroxy*iso*hexoic acid calculated from the results of Scheibler and Wheeler (*Ber.*, 1911, **44**, 2684) are $[M]^{20}_D$ −13·7° (in water) and $[M]^{20}_D$ −36·7° (in *N*-sodium hydroxide), whilst the ethyl ester gives $[M]^{20}_D$ −18·3°. Fischer and Moreschi (*Ber.*, 1912, **45**, 2447) find that *l*-α-hydroxyglutaric acid is feebly

lævorotatory in aqueous solution at 18°, and that the sodium salt gives $[M]_D^{20} - 14{\cdot}6°$. On the other hand, whilst *l*-α-hydroxy*iso*valeric acid is slightly lævorotatory in aqueous solution, the zinc salt in *N*-sodium hydroxide gives $[M]_D^{20} + 35{\cdot}4°$ (Fischer and Scheibler, *Ber.*, 1908, **41**, 2891). It thus seems very probable that *l*-α-hydroxy*iso*valeric acid possesses the same configuration as *d*-tartaric acid, but that *l*-α-hydroxy*iso*hexoic acid and *l*-α-hydroxyglutaric acid are enantiomorphously related to this acid. The conclusion is therefore drawn that *l*-lactic acid,* *l*-glyceric acid, *d*-malic acid, *d*-α-hydroxybutyric acid, *l*-α-hydroxy*iso*valeric acid, *d*-α-hydroxy*iso*hexoic acid, *d*-α-hydroxyglutaric acid, and *d*-β-phenyl-lactic acid all possess the same relative configurations as *d*-tartaric acid. These optically active acids will be referred to in the sequel as "*d*"- and their optical antipodes as "*l*"-aliphatic α-hydroxy-acids.

The remarkable effect on rotatory power which has been frequently noticed when a phenyl group is attached to the asymmetric carbon atom rendered it advisable to compare the influence of salts on the rotatory power of such a compound with that exerted on aliphatic compounds. Sodium chloride was found to increase the lævorotatory power of *l*-mandelic acid in aqueous solution from $[\alpha]_{gr.}^{14} - 188°$ ($c = 1{\cdot}6$) to $[\alpha]_{gr.}^{14} - 203°$ (4*N*-sodium chloride, $c = 1{\cdot}6$), and sodium bromide had a similar effect on ethyl *l*-mandelate, which gave $[\alpha]_{gr.}^{15} - 141°$ in methyl alcohol ($c = 10$) and $[\alpha]_{gr.}^{15} - 181°$ in *N*-methyl-alcoholic sodium bromide ($c = 10$). If the rules which have been established from a study of the simple aliphatic α-hydroxy-acids may be applied when a phenyl group is attached to the central carbon atom, it would follow that *l*-mandelic acid is related to *d*-tartaric acid. This conclusion receives support on reference to the rotations of some derivatives (esters, amide) from *l*-mandelic acid. The lævorotatory power of *l*-mandelic acid in aqueous solution diminishes on dilution, and the salts possess numerically lower molecular rotations than the free acid in aqueous solution. The lævorotatory powers of the acid in aqueous solution (Lewkowitsch, *Ber.*, 1883, **16**, 1567) and of the esters in the pure condition (J. W. Walker, *J. Physical Chem.*, 1909, **13**, 574) diminish with rise of temperature, and the molecular rotatory powers of the esters decrease numerically with increase of molecular weight—methyl ester $[M]_D^{20} - 276°$, ethyl ester $[M]_D^{20} - 226°$ (J. W. Walker, *loc. cit.*), *iso*butyl ester $[M]_D^{20} - 209°$ (Walden, *Zeitsch. physikal. Chem.*, 1895, **17**, 706). In all these respects, the behaviour of l-mandelic acid is opposite to that of *l*-malic acid.

* In this paper, the designations (*d*- or *l*-) of the optically active compounds mentioned are those usually given in the literature, and are not used to indicate the relative configurations of the compounds.

It must be repeated that the employment of this method cannot be regarded as wholly satisfactory unless the compounds and their derivatives are examined in a systematic manner under varying conditions, but it is shown later that there is confirmatory evidence that the conclusions which have been drawn with regard to the configurations of the active aliphatic α-hydroxy-acids are in all probability correct. It may be recalled that Frankland and Turnbull have shown the configurative relationships of the optically active esters of αβ-dichloropropionic acid by investigating the effect of temperature on their rotatory powers (T., 1914, **105**, 456), and that the present author has discussed the relative configurations of the optically active normal secondary alcohols on the basis of their optical rotation constants determined by Pickard and Kenyon (P., 1913, **29**, 357. Compare Kenyon, T., 1914, **105**, 2232). Pickard and Kenyon have suggested the employment of a "characteristic diagram" (Armstrong and Walker, *Proc. Roy. Soc.*, 1913, [*A*], **88**, 388) for determining whether a change of configuration has taken place in the formation of a derivative (P., 1913, **29**, 296).

α-Amino-acids and their Derivatives.

The author has previously shown that the optical rotatory powers of *l*-asparagine and *l*-aspartic acid are very susceptible to the influence of inorganic salts (T., 1915, **107**, 1509). Pfeiffer subsequently obtained similar results for *d*-alanine, the dextrorotatory power of which in aqueous solution is raised by the dissolution of lithium chloride or calcium chloride; thus, the addition of 5 grams of calcium chloride to 10 c.c. of an aqueous solution of *d*-alanine (10 per cent.) raised $[\alpha]_D$ from $+2{\cdot}10°$ to $+11{\cdot}85°$ (*Ber.*, 1915, **48**, 1938). For the sake of comparison with *l*-aspartic acid, the present author has determined the rotations of *d*-alanine in aqueous solutions of other salts (table VII).

TABLE VII.

The Influence of Inorganic Salts on the Optical Rotatory Power of d-*Alanine in Aqueous Solution.*

Solvent.	c	$\alpha^{15}_{gr.}(l=2)$.	$[\alpha]^{15}_{gr.}$
Water	10·0	+ 0·58°	+ 2·9°
Aqueous potassium chloride (*N*)	10·0	0·61	3·0
„ sodium chloride (*N*)	10·0	0·66	3·3
„ barium chloride (*N*)	10·0	0·70	3·5
„ barium bromide (4*N*)	10·0	0·96	4·8
„ hydrogen chloride (1·5 mols.)	5·78	2·06	17·8

Inasmuch as these results are similar to those observed for *l*-aspartic acid, which is dextrorotatory in aqueous solution at the

ordinary temperature, but becomes lævorotatory at higher temperatures, the influence of temperature on the rotatory power of *d*-alanine in aqueous solution has been studied and found to be quite similar to that on *l*-aspartic acid, a reversal in the sign of rotation being realised at about 70°.

The investigation has been extended to *d*-glutamic acid. The optical behaviour of this compound is parallel to that of *l*-aspartic acid; both these compounds are dextrorotatory in aqueous solution at the ordinary temperature, and elevation of temperature depresses the rotatory values, but whereas *l*-aspartic acid becomes lævorotatory at about 60°, it was not found possible to reverse the rotatory sign of *d*-glutamic acid in aqueous solution. The presence of neutral or acid salts in solution increases the dextrorotatory power of *d*-glutamic acid (table VIII).

TABLE VIII.

The Influence of Inorganic Salts on the Optical Rotatory Power of d-*Glutamic Acid in Aqueous Solution.*

Solvent.	p.	d^{25}.	$a^{25}_{gr.}(l=4)$.	$[a]^{25}_{gr.}$.
Water	1·50	1·003	+ 0·80°	+ 13·3°
Aqueous sodium chloride (N)	1·50	1·043	0·90	14·4
,, ,, ,, ($4N$)	1·51	1·152	1·10	15·8
,, potassium chloride (N)	1·53	1·050	0·95	14·8
,, barium chloride (N)	1·53	1·092	0·96	14·4
,, barium bromide ($4N$)	1·51	1·500	1·64	18·1
,, sodium hydroxide (1 mol.)	12·25	1·075	− 1·88	− 3·6
,, ,, ,, (2 mols.)	6·55	1·050	+ 3·22	+ 11·7
,, hydrogen chloride (1·5 mols.)	8·75			+ 37·4

A comparison of the rotatory powers of hydroxy-acids with those of their esters in the presence of neutral salts having shown that both classes of compounds are influenced in a similar manner, it was advisable to examine polarimetrically an ester of an amino-acid under various conditions, especially as such an examination might possibly throw some light on the constitution of amino-acids in aqueous solution. Accordingly, ethyl *l*-aspartate has been examined in various solvents. The lævorotatory power of this ester is increased by rise of temperature and reversed by dissolution in water or hydrochloric acid. The gradual addition of water (with which the ester is completely miscible) at first causes a rapid diminution of the lævorotation until $p=80$, when the solution is dextrorotatory; further dilution after $p=50$ has very little influence on the specific rotation. The addition of sodium or barium haloids increases the dextrorotatory power of the ester in aqueous solution, and sodium bromide reverses the lævorotatory power of the ester in methyl-alcoholic solution at 20°.

TABLE IX.

The Influence of Solvents on the Optical Rotatory Power of Ethyl l-Aspartate.

Solvent.	c.	$\alpha^{15}_{gr.}$ ($l = 2$).	$[\alpha]^{15}_{gr.}$.
None		− 6·34° ($l = 0·5$)	− 11·7°
Benzene	10·92°	− 2·75	− 12·6
Chloroform	11·02	− 2·13	−9·7
Acetone*	20·0	− 3·50	−8·8
Water	21·7	+ 1·83	+4·2
Water	12·25	1·03	4·2
Aqueous sodium chloride (4*N*)	10·81	1·44	6·7
Aqueous barium bromide (4*N*)	14·50	3·34	11 5
„ calcium chloride (5*N*)	13·21	3·84	14·5
„ hydrogen chloride (*N*)	11·37	2·73	12·0
Methyl alcohol	20·0	$\alpha^{20}_{gr.}$ − 0·19	$[\alpha]^{20}_{gr.}$ − 0·5
Methyl-alcoholic sodium bromide (*N*)	20·0	$\alpha^{20}_{gr.}$ + 1·72	$[\alpha]^{20}_{gr.}$ +4·3

* Ethyl *l*-aspartate reacts with acetone, the rotation changing from $\alpha_{gr.}$ − 3·50° to $\alpha_{gr.}$ − 56·6° ($c = 20$) in fifteen hours.

Finally, measurements made with benzoyl-*d*-alanine show that when the amino-group is displaced by the benzoylamino-group, the characteristic optical behaviour of the amino-acid disappears. For example, although benzoyl-*d*-alanine is only feebly dextrorotatory in aqueous solution ($[\alpha]^{15}_{gr.}$ + 0·3°, p=12), little alteration could be detected on raising the temperature ($[\alpha]^{47}_{gr.}$ + 0·2°; the specific rotation is slightly higher in *N*-potassium chloride ($[\alpha]^{20}_{gr.}$ + 0·4°, p = 11), but this result is due to the fact that the potassium salt of benzoyl-*d*-alanine is much more dextrorotatory than the free acid in aqueous solution. It thus appears that the effect of neutral salts on the rotatory powers of amino-acids is due to the presence of the amino-group in these compounds.

Now the elevation of the rotation of ethyl *l*-aspartate by dissolution in hydrochloric acid or water is probably due to the nitrogen atom becoming quinquevalent ($\cdot NH_3Cl$, $\cdot NH_3 \cdot OH$), and in the latter case there would probably exist in solution a mixture of the hydrated and non-hydrated forms of the amine. The rotatory values for the amino-acid and ester indicate similar constitutions in solution for both compounds, and it would thus appear that *l*-aspartic acid in aqueous solution consists mainly of the forms $CO_2H \cdot CH_2 \cdot CH(NH_2) \cdot CO_2H$ and $CO_2H \cdot CH_2 \cdot CH(NH_3 \cdot OH) \cdot CO_2H$, the former being lævorotatory and the latter dextrorotatory. The relative amount of the hydrated form would diminish with rise of temperature. Further work on the rotatory powers of amino-

acids and their esters would be of interest in this connexion. The presence of neutral salts influences not only the rotatory powers, but the solubilities of amino-acids and proteins in aqueous solution. Schiff (*Ber.*, 1884, **17**, 2929) observed that aspartic acid dissolves more readily in aqueous ammonium chloride than in water, and suggested that this was due to the amino-acid exercising its basic and acidic functions, the compounds yielding an equilibrium mixture of ammonium aspartate, aspartic acid hydrochloride, and unchanged ammonium chloride. Sakurai (P., 1894, **10**, 90) ascribed the formula $CH_2(NH_3{\cdot}NO_3){\cdot}CO_2K$ to a compound of glycine with potassium nitrate described by Boussingault (*Annalen*, 1841, **39**, 310). Although unable to isolate this compound, Pfeiffer and von Modelski succeeded in preparing a large number of compounds of amino-acids with the haloids of the alkali and alkaline earth metals, and also regarded these compounds as "amphi" salts possessing the formulæ $Me'O{\cdot}CO{\cdot}R{\cdot}NH_3X$ or

$$Me'' \begin{matrix} O{\cdot}CO{\cdot}R{\cdot}NH_3X \\ O{\cdot}CO{\cdot}R{\cdot}NH_3X' \end{matrix}$$

(*Zeitsch. physiol. Chem.*, 1912, **81**, 329; 1913, **85**, 1). This view was modified by Pfeiffer and Wittka, who regard the compounds of inorganic salts with amino-acids, carboxylic acids, esters, etc., as "molecular" compounds, without excluding the possibility that the halogen atom of the inorganic salt is combined with the amino-group of an amino-acid in the form of an ammonium salt (*Ber.*, 1915, **48**, 1289). Pfeiffer has also brought forward strong evidence that the compounds of amino-acids with neutral salts are capable of existence in aqueous solution (*Ber.*, 1915, **48**, 1938). Inasmuch as the amino-acids are amphoteric electrolytes possessing very small acid and basic constants (for alanine $K_a = 1{\cdot}9 \times 10^{-10}$, $K_b = 5{\cdot}1 \times 10^{-12}$), it does not seem possible for the halogen of the salts to be combined in the "ammonium" salt form, nor for compounds of the "amphi" salt type to exist to an appreciable extent in aqueous solution. Such an objection cannot be raised if the compounds are regarded as "molecular" compounds with the metallic atom co-ordinated with the oxygen of the carboxyl group or with the nitrogen of the amino-group (Pfeiffer, *loc. cit.*). The observed regularities in the effects of barium, calcium, and sodium haloids make it appear probable that the influence of salts on the rotatory powers of hydroxy- and amino-compounds is due to the same cause. It may therefore be assumed that this influence is due to combination of the salts with the optically active compounds in question, the latter reacting with the salts in consequence of the residual affinity of the oxygen and nitrogen atoms in the alkylic

hydroxyl and amidogen radicles respectively. It is thus no longer necessary to explain the alterations in rotatory power caused by the presence of neutral salts by means of the recently revived hypothesis of Arndtsen that the changes in rotatory power are due to a displacement in the equilibrium of hypothetical isodynamic forms of the active compound.

An examination of table X shows that there are certain regularities in the rotatory powers of the derivatives from the optically active α-amino-acids. The rotatory powers of the hydrochlorides of those varieties of the active amino-acids in this table are in every case more positive than those of the amino-acids in aqueous solution, and in general the molecular rotations of the potassium salts of the benzoylamino-acids are more positive than those of the hydrochlorides of the amino-acids. The aminoacylglycines possess relatively high positive rotations in aqueous solution, whilst the glycyl derivatives of the amino-acids in question are usually lævorotatory, glycyl-*l*-phenylalanine being a noticeable exception. Similar regularities are observable in the recorded values for the diketopiperazines, β-naphthalenesulphonyl, and *N*-methyl derivatives of the same amino-acids.

Fischer and Raske (*Ber.*, 1907, **40**, 3717) have transformed *l*-serine into *l*-β-chloro-α-aminopropionic acid, and the latter into *d*-alanine, without displacing groups directly attached to the asymmetric carbon atom, and they have pointed out that the hydrochlorides of these amino-acids possess more positive rotatory powers than the configuratively related parent acids. A similar regularity is evident in the rotatory powers of the related compounds *l*-asparagine and *l*-aspartic acid, and the author maintains that *the rotatory values for the amino-acids and their derivatives in table X indicate that all these compounds possess the same relative configurations*. The influence of temperature on the rotatory powers of *l*-asparagine, *l*-aspartic acid (T., 1915, **107**, 1509), and *d*-glutamic acid is similar to that on *d*-alanine in aqueous solution, and the rotatory powers of these compounds are increased by the addition of sodium or barium haloids. The similarity between *l*-aspartic acid and *d*-glutamic acid is shown admirably by the curves of Andrlík (*Zeitsch. Ver. deut. Zuckerind.*, 1903, 948) and Wood (T., 1914, **105**, 1988) illustrating the effect of varying amounts of bases on the rotations of these acids. It should also be pointed out that those amino-acids which have been obtained from protein occur in the optically active varieties denoted in table X. Moreover, Ehrlich observed that when certain inactive amino-acids were subjected to the action of yeast in sugar solutions, the forms which survived attack were the enantiomorphs of the naturally occurring

Table X.

The Optical Rotatory Powers ($[\alpha]_D^{20}$) *of α-Amino-acids and of certain Derivatives from them.*

Amino-acid.	Water.	Hydrochloric acid.	Benzoylamino-acid (in KOH,aq.).	Aminoacylglycine (in water).	Glycylamino-acid (in water).	Hydantoin.*
d-Alanine[1]	+ 2·7°	+ 14·3°	+ 36·5°	+ 50·2°	− 50·0°	+ 50·6° (water)
l-Serine[2]	− 6·8	+ 14·4	+ 43·6 (in NaOH,aq.) (*p*-nitrobenzoyl)	—	—	—
l-β-Chloro-α-aminopropionic acid[3]	− 15·5	+ 0·9	—	—	—	—
d-α-Aminobutyric acid[4]	+ 8·0	+ 19·6	+ 30·7 (in NaOH,aq.)	+ 86·4 (K) + 26·8 (A & C)	− 20·3	—
d-Valine[5]	+ 6·4	+ 28·7	—	+ 90	− 19·7	− 97·5 (phenylhydantoin in alcohol).
d-α-Aminohexoic acid[6]	—	+ 23·0	+ 21·9	—	—	—
l-Leucine[7]	− 10·3	+ 15·6	+ 6·6 (in NaOH,aq.)	+ 85·5	− 35·0	− 68·2 (in NaOH,aq.)

* Hydantoins, Dakin & Dudley, *J. Biol. Chem.*, 1913, **17**, 29; 1914, **18**, 48; T., 1915, **107**, 434.

[1] Fischer, *Ber.*, 1905, **38**, 2914; 1906, **39**, 453; 1907, **40**, 943.

[2] Fischer and Jacobs, *Ber.*, 1906, **39**, 2942; Fischer and Raske, *Ber.*, 1907, **40**, 3717.

[3] Fischer and Raske, *loc. cit.*

[4] Fischer and Mouneyrat, *Ber.*, 1900, **33**, 2383; Koelker, *Zeitsch. physiol. Chem.*, 1911, **73**, 312; Abderhalden and Chang, *ibid.*, 1912, **77**, 471.

[5] Fischer, *Ber.*, 1906, **29**, 2320; Fischer and Scheibler, *Annalen*, 1908, **363**, 136.

[6] Fischer and Hagenbach, *Ber.*, 1901, **34**, 3764.

[7] Fischer, *Ber.*, 1900, **33**, 2370; *Ber.*, 1906, **39**, 2893; Fischer and Steingroever, *Annalen*, 1909, **365**, 167.

TABLE X.—(*continued*).

The Optical Rotatory Powers ($[\alpha]_D^{20}$) *of α-Amino-acids and of certain Derivatives from them.*

Amino-acid.	Water.	Hydrochloric acid.	Benzoylamino-acid (in KOH,aq.).	Aminoacylglycine (in water).	Glycylamino-acid (in water).	Hydantoin.*
*d-iso*Leucine[8]	+ 11·3°	+ 40·6°	+ 26·4° (in NaOH,aq.)	+ 33·6°	− 14·7°	—
l-Asparagine[9]	− 4·9	+ 28·5	—	—	− 6·4	—
l-Aspartic acid[10]	+ 4·3	+ 25·7	+ 37·4	—	+ 11·1	− 125 (in NaOH,aq.).
d-Glutamic acid[11]	+ 9·9	+ 30·8	+ 18·7	—	− 6·3	− 79 (in NaOH,aq)
l-Phenylalanine[12]	− 35·3	− 7·1	+ 17·1	+ 54·2	+ 41·4	− 96·4 (in 50 per cent. alcohol).
l-Tyrosine[13]	—	− 8·6	+ 19·2	—	—	− 143 (in NaOH,aq.)

* Hydantoins, Dakin and Dudley, *J. Biol. Chem.*, 1913, **17**, 29; 1914, **18**, 48; T., 1915, **107**, 434.
[8] Locquin, *Bull. Soc. chim.*, 1907 [iv], **1**, 595; Abderhalden, Hirsch, and Schuler, *Ber.*, 1909, **42**, 3394.
[9] Fischer and Koenigs, *Ber.*, 1904, **37**, 4585.
[10] Fischer, *Ber.*, 1899, **32**, 2451; Fischer and Fiedler, *Annalen*, 1910, **375**, 181.
[11] Fischer, Kropp, and Stahlschmidt, *Annalen*, 1909, **365**, 189.
[12] Fischer and Mouneyrat, *loc. cit.*; Fischer and Schoeller, *Annalen*, 1907, **357**, 1.
[13] Fischer, *Ber.*, 1899, **32**, 3638.

forms. The configurations of the constituent amino-acids also appear to condition the hydrolysis of polypeptides by enzymes; thus only those compounds containing the naturally occurring optically active forms of the amino-acids are hydrolysed by trypsin (Fischer and Abderhalden, *Zeitsch. physiol. Chem.*, 1907, **51**, 264). The optically active amino-acids appearing in table X may therefore be conveniently termed the "*l*"-aliphatic α-amino-acids.

It may be recalled that *l*-phenylaminoacetic acid was obtained by Ehrlich by the action of yeast on the optically inactive amino-acid. The rotatory values for this acid recorded by Fischer and Weichhold (*Ber.*, 1908, **41**, 1293) are $[\alpha]_D^{20}$ −112·6° (water), −158° (*N*-hydrochloric acid), and −260° for the formyl derivative, values which may be compared with those for *l*-phenylalanine, $[\alpha]_D^{20}$ −35·3° (water), −7·1° (hydrochloric acid), and +75·2° for the formyl compound. These results appear to show that *d*-phenyl-aminoacetic acid is related configuratively to the active amino-acids in table X.

The α-Halogen Acids.

The optically active halogen acids may be obtained from the active hydroxy-acids by phosphorus haloids or thionyl chloride, from the active amino-acids by nitrosyl chloride (or bromide), or by the resolution of the inactive compounds. The racemisation which usually accompanies reactions involving the displacement of groups attached to the asymmetric carbon atom and the reactivity of the halogen towards bases, frequently make it difficult to obtain the active forms of the halogen acids in a state of purity. There are necessarily fewer derivatives of the halogen acids than of the hydroxy- or amino-acids, and there is no doubt that some of the values given in the literature for halogen acids and derivatives from them are numerically lower than those for the pure active compounds. The values in table XI for certain *d*-α-halogen acids indicate the great probability that all these compounds possess the same configurations. Inasmuch as these optically active halogen acids are all dextrorotatory, their usual designation *d*- may also be used to indicate their configurative similarity to one another (see footnote, p. 547).

The rotatory powers of the esters of the *d*-α-halogen-propionic and -succinic acids diminish with increase of molecular weight, and it appears from the table that the glycines possess higher molecular rotatory powers than the parent acids. The specific rotatory power of *d*-bromopropionic acid diminishes with rise of temperature (Ramberg), as is also the case for methyl and ethyl *d*-α-chloropropionates (J. W. Walker) and for methyl *d*-bromosuccinate

TABLE XI.

The Specific Rotations ($[\alpha]_D^{20}$) *of certain* d-α-*Halogen Acids and their Derivatives.*

	Acid.	Methyl ester.	Ethyl ester.	Propyl ester	Bromoacyl-glycine.	References.
d-α-Chloropropionic acid	+ 14°*	+26·8° (at 5°)	+19·9 (at 5°)	+11·0° (at 6°)	—	Frankland and Garner, T., 1914, **105**, 1101; J. W. Walker, T., 1895, **67**, 918.
d-α-Bromopropionic acid	+ 29·0	+42·6	+35·5	+22	+35·3 (water)	J. W. Walker, *loc. cit.*, Ramberg, *Annalen*, 1909, **370**, 234; Fischer, *Ber.*, 1907, **40**, 489.
d-α-Bromo*iso*valeric acid	+ 9·0 (water); 22·8 (benzene)	—	—	—	+47·5 (alcohol)	Fischer and Scheibler, *Ber.*, 1908, **41**, 889, 2891.
d-α-Bromo*iso*hexoic acid	+ 49·4	—	+50	—	+62 (alcohol)	Fischer and Carl, *Ber.*, 1906, **39**, 3998.
d-α-Bromo-β-methylvaleric acid	+ 26·5 (benzene)	—	—	—	+64·4 (alcohol)	Abderhalden, Hirsch, and Schuler, *Ber.*, 1909, **42**, 3394.
d-α-Bromo-β-phenylpropionic acid	+ 10·4	—	+9	—	+14·6 (alcohol)	Senter, Drew, and Martin, this vol., p. 158; Fischer and Carl, *loc. cit.*; Fischer and Schoeller, *Annalen*, 1907, **357**, 1
d-Chlorosuccinic acid	+ 21·7 (water); 55·7 (ethyl acetate)	+42·3	+32·7	+25	—	Walden, *Ber.*, 1896, **29**, 1689; McKenzie and Barrow, T., 1911, **99**, 1919.
d-Bromosuccinic acid	+ 41·8 (water); 76·5 (ethyl acetate)	+51·2	+41·0	+38·0	—	Walden, *Ber.*, 1895, **28**, 1290, *Zeitsch. physikal. chem.*, 1895, **17**, 264.
d-Dichlorosuccinic acid.....	+ 80·4 (ethyl acetate)	—	+66 (chloroform)	—	—	Holmberg, *Svensk. Kem. Tid.*, 1912; Darzens and Séjourné, *Compt. rend.*, 1912, **154**, 1615.
d-Dibromosuccinic acid	+ 70 (water)*; 148 (ethyl acetate)	—	—	—	—	Holmberg, *Svensk. Kem. Tid.*, 1911; McKenzie, T., 1912, **101**, 1196.

* Approximate values by calculation.

(Walden). On the other hand, Senter, Drew, and Martin find that the lævorotatory power of *l*-α-bromo-β-phenylpropionic acid is increased by rise of temperature.

It has been shown by Frankland and Turnbull (*loc. cit.*) that the optically active methyl αβ-dichloropropionate obtained by the action of phosphorus pentachloride on methyl *d*-glycerate is dextrorotatory, whereas the higher esters are lævorotatory. It would thus seem that these esters are related to the *d*-halogen acids in table XI, the temperature coefficients of the esters in question being similar in character to that of *d*-α-bromo-β-phenylpropionic acid. The rotations of the *d*-phenylhalogenacetic acids are considerably higher in benzene solution than in aqueous solution, and the specific rotation of the ethyl ester appears to be lower than that of the free acid (McKenzie and Barrow, T., 1911, **99**, 1919); moreover, the rotatory powers of the methyl and ethyl esters diminish with rise of temperature (J. W. Walker). These facts indicate that the dextrorotatory acids are configuratively related to *d*-chloropropionic acid.

The Relationship between the Optically Active α-Halogen Acids and α-Amino-acids.

The foregoing considerations render it possible to determine whether the conversions of the optically active α-amino-acids into the halogen acids which have been effected by nitrosyl haloids are or are not similar in stereochemical character. It has often been assumed that the action of nitrosyl haloids on the active amino-acids is always of the same character, but it is certain that a given reagent does not invariably act in the same way on compounds of similar type. The following conclusions may be drawn from the relationships which have been established for the active α-amino-acids and α-bromo-acids respectively:

(*a*) The transformations *d*-alanine ⟶ *l*-bromopropionic acid, *l*-aspartic acid ⟶ *l*-chlorosuccinic acid (or *l*-bromosuccinic acid), *d*-valine ⟶ *l*-α-bromo*iso*valeric acid, *l*-leucine ⟶ *l*-α-bromo*iso*-hexoic acid, *d-iso*leucine ⟶ *l*-α-bromo-β-methylvaleric acid, and *l*-phenylalanine ⟶ *l*-α-bromo-β-phenylpropionic acid (by the action of nitrosyl haloids), are all of the same stereochemical character, that is to say, they are either all "normal" or all "abnormal" reactions. Inasmuch as *d*-glutamic acid and *d*-α-aminobutyric acid are, according to the author, related to the above amino-acids, it is almost certain that the changes *d*-glutamic acid ⟶ *l*-α-chloro-glutaric acid ($[\alpha]_D^{25}$ −12·5° in water) and *l*-α-aminobutyric acid ⟶ *d*-α-bromobutyric acid ($[\alpha]_D$ +15·4°, Abderhalden and Chang, *loc.*

cit.) are also of this type (for references, see Frankland, T., 1913, **103**, 728).

(*b*) The action of nitrosyl bromide on esters of *d*-alanine, *l*-aspartic acid, *l*-leucine, and *l*-phenylalanine is opposite in character to that of this reagent on the amino-acids mentioned in paragraph (*a*).

(*c*) The action of ammonia on *l*-α-bromopropionic acid (or ester), *l*-bromosuccinic acid, *l*-α-bromo*iso*valeric ester, *l*-α-bromo*iso*hexoic acid (or ester), *l*-α-bromobutyric acid or *l*-α-bromo-β-phenylpropionic acid is opposite to that of nitrosyl bromide on the amino-acids mentioned in paragraph (*a*). Fischer has shown that the action of potassium phthalimide on ethyl *l*-α-bromopropionate (*Ber.*, 1907, **40**, 489), that of trimethylamine on *d*-α-bromopropionic acid (*Ber.*, 1907, **40**, 5000), and that of methylamine on *l*-α-bromopropionic acid, *d*-α-bromo*iso*hexoic acid, or *d*-α-bromo-β-phenylpropionic acid, all take place in the same stereochemical sense as the action of ammonia on the same compounds (Fischer and von Mechel, *Ber.*, 1916, **49**, 1355). It is exceedingly probable that the numerous examples of the action of ammonia on the active α-bromoacyl derivatives of amino-acids which have been investigated by Fischer and Abderhalden are all of this type.

(*d*) The action of ammonia on *l*-α-bromo*iso*valeric acid or on *l*-α-bromo-β-methylvaleric acid is the reverse of that of the same reagent in the examples given in paragraph (*c*).

In order to decide in which of the above reactions a change of configuration takes place, it becomes necessary to ascertain whether the active α-amino-acids in table X possess the same relative configurations as the *d*-halogen acids in table XI. Although these two classes of compounds can scarcely be considered to be "similarly constituted," it is desirable that a comparison of the rotatory powers of their derivatives should be made in this connexion. Unfortunately, there are very few similar classes of derivatives of the amino-acids on the one hand and of the halogen acids on the other the rotatory powers of which are available for a comparative study of these compounds. The most complete series of derivatives are the α-bromoacyl- and the α-aminoacyl-amino-acids. It is evident from table XII that there is a close relationship between the values for the aminoacyl derivatives and the bromoacyl derivatives from which they are obtained, and it appears to the author that this relationship indicates the great probability that the amino-derivatives are configuratively related to the bromo-derivatives in question. For example, *d*-α-bromopropionyl-*l*-alanine ($[\alpha]_D$ +68·2) is related to *d*-alanyl-*l*-alanine ($[\alpha]_D$ +68·9), and not to *l*-alanyl-*l*-alanine ($[\alpha]_D$ +21·6). If, for the purpose of this

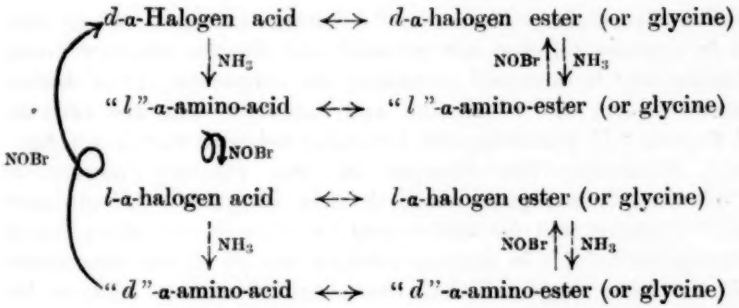
Table XII.

The Optical Rotatory Powers ($[\alpha]_D^{20}$) *of certain α-Bromoacyl and α-Aminoacyl Derivatives of the α-Amino-acids.*

Amino-acid.	Amino-acid.	Chloro-acetyl-amino-acid.	Glycyl-amino-acid.	*d*-α-Bromo-propionyl-amino-acid.	*d*-Alanyl-amino-acid.	*d*-α-Bromo-*iso*hexoylamino-acid.	*l*-Leucylamino-acid	References.
Glycine	—	—	—	+ 38·3°	+ 50·2°	+ 62·0° (in alcohol)	+ 86·0°	Fischer, *Ber.*, 1908, **41**, 850; 1906, **39**, 2911.
d-Alanine	+ 2·7°	− 45°	− 50°	− 16·5	− 21·6	+ 23·3 (in alcohol)	+ 23·5 (in methyl alcohol)	Fischer, *Ber.*, 1906, **39**, 453; Fischer and Schulze, *Ber.*, 1907, **40**, 943.
l-Alanine	− 2·7	+ 45	+ 50	+ 68·2	+ 68·9	—	—	Fischer and Raske, *Ber.*, 1906, **39**, 3989.
l-Leucine	− 10·3	− 13·8	− 35·2	+ 2·0 (in alcohol)	− 17·0	+ 16·2 (in ethyl acetate)	− 13·4 (in *N*-NaOH)	Fischer, *Ber.*, 1907, **40**, 1754.
d-Leucine	+ 10·3	+ 13·8	+ 35·2	—	—	+ 35 (in ethyl acetate)	+ 68·9 (in *N*-HCl)	Fischer and Koelker, *Annalen*, 1907, **354**, 39.
*d-iso*Leucine ...	+ 10·5	+ 25·0 (in alcohol)	− 14·7	+ 24·5 (in alcohol)	+ 6·1 (in HCl)	+ 49 (in ethyl acetate)	+ 18·1	Abderhalden, Hirsch, and Schuler, *Ber.*, 1909, **42**, 3394.
*l-iso*Leucine ...	− 10·5	− 25·0 (in alcohol)	+ 14·7	—	—	+ 19 (in alcohol)	+ 53·1	Abderhalden and Schuler, *Ber.*, 1910, **43**, 907.

The values in this table are for the specific rotations in aqueous solution unless stated otherwise.

discussion, the active amino-acids in table X be denoted by the designation "*l*," it follows that the "*l*" amino-acids possess the same configuration as the *d*-halogen acids,* and that the action of ammonia on the above halogen acids (with the exception of α-bromo*iso*valeric acid and α-bromo-β-methylvaleric acid) or their derivatives does not cause a configurative change. It may be mentioned in this connexion that Scheibler has conclusively shown that the action of ammonia on *l*-ββ′-iminodibutyric acid, yielding *l*-β-aminobutyric acid, is a "normal" action (*Ber.*, 1912, **45**, 2272). The transformations of the aliphatic α-amino-acids (including phenylalanine), with the exception of valine and *iso*leucine, may be represented by the following scheme (compare Frankland, T., 1913, **103**, 741):



The scheme for "*l*"-valine and "*l*"-*iso*leucine is similar, except that the action of ammonia on the free bromo-acids is assumed to be "abnormal." *iso*Leucine contains two asymmetric carbon atoms, and a true Walden inversion cannot be effected, but the transformations involved are similar to those for valine.

The Relationship between the Optically Active α-Amino- and α-Hydroxy-acids.

It is clear from the relationships which have been established for the amino-acids and hydroxy-acids, respectively, that the trans-

* It appears advisable to retain for the present the designation *d*- for the dextrorotatory α-halogen acids to denote their configurative similarity to one another. If the above view that these dextrorotatory α-halogen acids are related configuratively to the "*l*"-α-amino-acids is correct, it would be preferable to indicate their configurations by the prefix "*l*-." It may be mentioned here that it is not possible to denote the relative configuration of a given optically active compound (containing only one asymmetric carbon atom) always by means of the same prefix (Clough, P., 1913, **29**, 359).

formations (effected by nitrous acid) *d*-alanine → *d*-lactic acid, *l*-serine → *d*-glyceric acid, *d*-valine → *d*-α-hydroxy*iso*valeric acid, *l*-leucine → *l*-α-hydroxy*iso*hexoic acid, *l*-aspartic acid → *l*-malic acid, *d*-glutamic acid → *l*-α-hydroxyglutaric acid, and *l*-phenylalanine → *l*-β-phenyl-lactic acid (Clough, unpublished) are all of the same stereochemical type. It is not possible with the data at present available to make a satisfactory comparison of the rotatory powers of the active hydroxy-acids with those of the active amino-acids. The rotatory powers of very few α-amino-esters have been determined, and of only two hydroxyacylglycines. There are, however, certain similarities which seem to indicate that the "*l*"-α-amino-acids possess the same relative configurations as the "*l*"-hydroxy-acids (which are enantiomorphously related to *d*-tartaric acid).

The dextrorotatory powers of "*l*"-lactic acid and "*l*"-glyceric acid in aqueous solution are reversed and the lævorotatory power of *l*-malic acid is increased on raising the temperature; the dextrorotatory powers of "*l*"-alanine and *l*-aspartic acid are reversed and that of "*l*"-glutamic acid is diminished with rise of temperature. Moreover, the changes in the rotatory powers of "*l*"-alanine, *l*-asparagine, *l*-aspartic acid (or ester), "*l*"-glutamic acid, "*l*"-lactic acid (or ester), and *l*-malic acid (or ester) caused by inorganic haloids in aqueous solution are all in the same sense. It is therefore suggested that the action of nitrous acid on the active aliphatic α-amino-acids is a "normal" action.

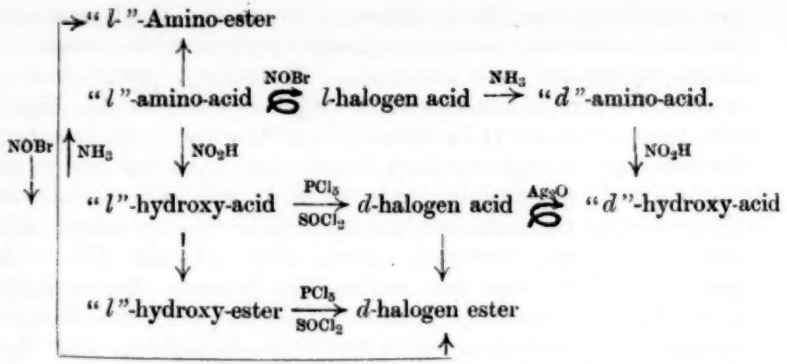
The Relationship between the Optically Active α-Hydroxy- and α-Halogen Acids.

The conclusions that have been drawn regarding the configurative relationships of the hydroxy-acids on the one hand and of the halogen acids on the other make it appear almost certain that the conversions of "*l*"-lactic acid (or ester) by phosphorus haloids or thionyl chloride into *d*-halogen-propionic acids (or esters), *l*-malic acid (or esters) by phosphorus pentachloride or thionyl chloride into *d*-chlorosuccinic acid (or esters), ethyl *l*-α-hydroxy-*iso*hexoate by phosphorus and bromine into ethyl *d*-α-bromo*iso*-hexoate, and of ethyl *d*-tartrate by thionyl chloride into ethyl *l*-dichlorosuccinate, are reactions of the same stereochemical character. When it is remembered that the specific rotatory powers of the *d*-halogen esters diminish as the homologous series are ascended, and that the rotatory powers of the *d*-bromo-esters are more positive than those of the corresponding chloro-esters, it

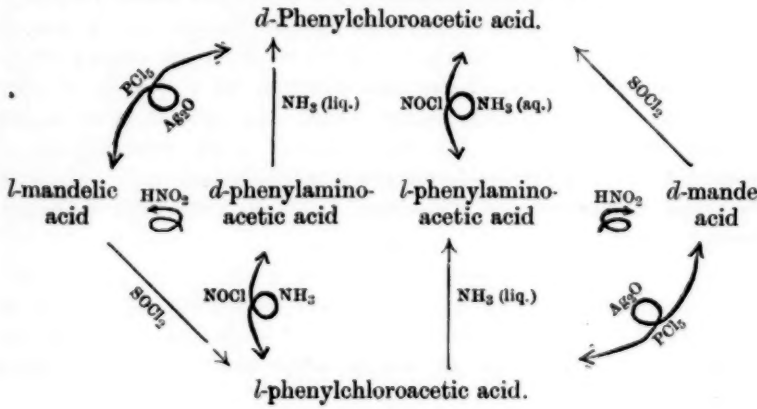
is not surprising that the lævorotatory esters of "*l*"-glyceric acid yield, on treatment with phosphorus pentachloride, esters of **αβ**-dichloropropionic acid diminishing in rotatory power from a positive value for the methyl ester to negative values for the higher esters, and that *iso*butyl *l*-**α**-hydroxybutyrate yields a lævorotatory chloro-ester but a dextrorotatory bromo-ester, these halogen esters being derived, presumably, from **α**-chloro- and **α**-bromo-butyric acids possessing the same configurations as *d*-chloropropionic acid (Guye and Jordan, *Bull. Soc. chim.*, 1896, [iii], **15**, 495). It appears probable that the relationship between the optically active aliphatic normal secondary alcohols and the halogen compounds prepared from them by hydrogen haloids, and that between *l*-**β**-hydroxybutyric acid (or ester) and *d*-**β**-chlorobutyric acid (or ester) obtained from it by phosphorus pentachloride, are also of the same character. There is little doubt that thionyl chloride would react with these hydroxy-compounds in the same manner as hydrogen haloids or phosphorus pentachloride respectively.

If it is assumed that the "*l*"-amino-acids are related to the *d*-halogen acids and also to the "*l*"-hydroxy-acids, it follows that the "*l*"-hydroxy-acids are of the same configuration as the *d*-halogen acids. It may be recalled that the temperature–rotation curves for ethyl *d*-bromopropionate and ethyl *d*-bromosuccinate are similar in character to those of *d*-("*l*-")lactic acid (or ester) and *l*-malic acid (or ester). On the other hand, the influence of temperature on methyl *d*-**αβ**-dichloropropionate is opposite to that on methyl "*l*"-glycerate, from which it is prepared.

The fact that the rotatory powers of the *d*-halogen esters diminish as the carbalkyloxy-groups increase, whilst the rotations of the *d*-hydroxy-esters increase as the series is ascended (at least for the early members), is in accordance with the above view. It may therefore be assumed that the action of phosphorus haloids and of thionyl chloride on the aliphatic **α**-hydroxy-acids (or esters) which have been investigated is not accompanied by a change of configuration. The following scheme would then include most of the changes which have so far been realised with **α**-derivatives of propionic acid, butyric acid, succinic acid, *iso*hexoic acid, and (with the possible exception of the action of thionyl chloride) **β**-phenylpropionic acid:



It has been suggested above that *l*-mandelic acid is configuratively allied to *d*-malic acid, that the *l*-phenyl-halogen-acetic acids are related to *l*-chlorosuccinic acid, and that *l*-phenylaminoacetic acid has a similar configuration to that of *d*-aspartic acid. Inasmuch as it has been assumed that *l*-chlorosuccinic acid is configuratively related to *d*-malic acid and to *d*-aspartic acid, it would follow that *l*-mandelic acid, the *l*-phenyl-halogen-acetic acids, and *l*-phenylaminoacetic acid all possess the same relative configurations. In any case, it is almost certain from the rotatory powers of the latter compounds that their common designation (*l*-) may also be used to imply a similar configurative relationship. The following scheme, then, represents most of the transformations of the derivatives of phenylacetic acid, and also (as far as they have been studied) those of the β-derivatives of β-phenylpropionic acid and of the α-derivatives of α-phenylpropionic acid, with the exception of those reactions of the latter in which complete racemisation occurs. The reactions which have been effected with esters of the acids are likewise in conformity with this scheme.



Summary of Conclusions.

(*a*) A comparison of the optical rotatory powers of the acids commonly written *l*-lactic acid, *l*-glyceric acid, *d*-malic acid, and *d*-tartaric acid (which possess the same relative configurations), and of derivatives from them, has led the author to assume that *the optical rotatory powers of similarly constituted compounds possessing the same configuration are, in general, influenced similarly by the same changes in the external conditions and also by the introduction of the same substituent into a given radicle attached to the asymmetric carbon atom.*

(*b*) The rotatory powers of the above four acids, and also of *d*-α-hydroxybutyric acid, *l*-α-hydroxy*iso*valeric acid, *d*-α-hydroxy*iso*hexoic acid, *d*-α-hydroxy-β-phenylpropionic acid, *d*-α-hydroxyglutaric acid and their derivatives, indicate that all these acids possess the same relative configurations. For the sake of convenience, the designation "*d*" has been used to denote the configurations of these compounds.

(*c*) Similarly, it is assumed that the naturally occurring α-amino-acids, commonly denoted as *d*-alanine, *l*-serine, *l*-aspartic acid, *d*-valine, *l*-leucine, *d-iso*leucine, *d*-α-aminobutyric acid, *d*-glutamic acid, *l*-phenylalanine, and *l*-tyrosine, all possess the same configurations. The configurations of these compounds have been denoted by the symbol "*l*."

(*d*) The dextrorotatory (*d*-) α-halogen acids which have been isolated are assumed to be configuratively similar compounds.

(*e*) A comparison of the rotatory powers of the optically active α-bromoacyl-amino-acids with those of the α-aminoacyl-amino-acids leads to the view that the amino-acids mentioned in paragraph (*c*) are related configuratively to the halogen acids mentioned in paragraph (*d*).

(*f*) It is suggested that the "*d*"-hydroxy-acids are enantiomorphously related to the "*l*"-amino-acids, and therefore to the *d*-halogen acids.

(*g*) The lævorotatory compounds, *l*-mandelic acid, *l*-phenylchloroacetic acid, and *l*-phenylaminoacetic acid, are assumed to possess the same configurations.

Experimental Data.

l-*Lactic Acid.*

The aqueous lactic acid was obtained by the hydrolysis of methyl *l*-lactate by boiling with ten times its weight of water for six

hours, and subsequent distillation of the methyl alcohol. This specimen contained 92 per cent. of *l*-lactic acid and 8 per cent. of *d*-lactic acid.

$p = 10{\cdot}73$.

t	15°.	18°.	36°.	52°.	62°.	70°.	15°.
d^t	1·03	1·03	1·02	1·01	1·01	1·00	1·03
$\alpha^t_{gr.}(l=4)$	− 0·95°	− 0·88°	− 0·32°	± 0·00°	+ 0·18°	− 0·30°	− 0·95°
$[\alpha]^t_{gr.}$	− 2·2°	− 2·0°	− 0·7°	± 0·0°	+ 0·4°	+ 0·7°	− 2·2°

A specimen of *l*-lactic acid prepared from zinc *l*-lactate showed similar behaviour.

Methyl l-*Lactate.*

This ester was prepared from zinc *l*-lactate, obtained from a dextrorotatory lactic acid syrup, which gave $\alpha_D(l=1) + 5{\cdot}2$, by Patterson and Forsyth's method (T., 1913, **103**, 2263). The specimen contained about 5 per cent. of methyl *d*-lactate.

	d^t.	$\alpha^t_D(l=1)$.	$\alpha^t_{gr.}$.	$\alpha^t_{vi.}$.	$[\alpha]^t_D$.	$[\alpha]^t_{gr.}$.	$[\alpha]^t_{vi.}$.*
15°	1·097	+ 7·96°	+9·05°	+11·95°	+ 7·26°	+8·25°	+10·89°
20	1·093	+ 8·15	9·17	12·25	7·46	8·39	11·21

* The rotations recorded in this paper and in the previous paper (*loc. cit.*) for mercury violet light ($[\alpha]_{vi.}$) are for $\lambda = 4078$.

Methyl l-*Lactate in Water.*

p.	d^{20}.	$\alpha^{20}_D(l=1)$.	$\alpha^{20}_{gr.}$.	$\alpha^{20}_{vi.}$.	$[\alpha]^{20}_D$.	$[\alpha]^{20}_{gr.}$.	$[\alpha]^{20}_{vi.}$.
100	1·093	+ 8·15°	+9·17°	+ 12·25°	+ 7·46°	+ 8·39°	+ 11·21°
80·0	1·086	3·60	3·81	3·90	4·1	4·4	4·5
50·9	1·063	1·16	1·34	0·54	2·1	2·5	1·0
20·0	1·026	0·72 ($l=2$)	0·73	− 0·08	1·8	1·8	− 0·2
10·0	1·012	0·27 ($l=2$)	0·29	− 0·10	1·3	1·4	− 0·5
5·36	1·005	0·28 ($l=4$)	0·30	− 0·30	1·3	1·4	− 0·9

d-*Alanine in Water.*

The specimen employed was prepared from silk by Fischer's method (*Ber.*, 1906, **39**, 462).

$p = 5{\cdot}85$.

t	13°.	16°.	29°.	40°.	64°.	74°.	80°.
d	1·02	1·02	1·01	1·01	1·00	1·00	1·00
$\alpha^t_{gr.}(l=4)$	+ 0·74°	0·68°	0·56°	0·40°	0·04°	− 0·04°	− 0·15°
$[\alpha]^t_{gr}$	+ 3·1°	2·9°	2·4°	1·7°	0·2°	− 0·2°	− 0·6°

$p = 9{\cdot}81$.

t	15°.	20°.	30°.	45°.	60°.	72°.
d^t	1·03	1·03	1·03	1·02	1·02	1·01
$\alpha^t_{gr.}(l=4)$	+ 1·41°	1·32°	1·10°	0·77°	0·48°	0·29°
$[\alpha]^t_{gr.}$	+ 3·5°	3·3°	2·7°	1·9°	1·2°	0·7°

d-*Alanine in Aqueous Sodium Hydroxide* (1 mol.).

$p = 7{\cdot}79$, d^{15} 1·045, $\alpha^{15}_{gr.}$ ($l = 2$) +1·06°, $[\alpha]^{15}_{gr.}$ +6·5°.
$p = 1{\cdot}61$, d^{15} 1·01, $\alpha^{15}_{gr.}$ ($l = 4$) +0·38°, $[\alpha]^{15}_{gr.}$ +5·8°.

d-*Alanine in Hydrochloric Acid.*

$p = 8{\cdot}098$ (1 mol. HCl); d^{15} 1·036, α^{15}_{D} ($l = 2$) +2·40°, $\alpha^{15}_{gr.}$ +2·88°, $[\alpha]^{15}_{D}$ +14·3°, $[\alpha]^{15}_{gr.}$ +17·1°.

$p = 5{\cdot}605$ (1·5 mols. HCl); d^{15} 1·033, α^{l}_{D} ($l = 2$) +1·70°, $\alpha^{15}_{gr.}$ +2·06°, $[\alpha]^{15}_{D}$ +14·7°, $[\alpha]^{15}_{gr.}$ +17·8°.

Ethyl l-*Aspartate.*

This ester was prepared by Fischer's method (*Ber.*, 1901, **34**, 452).

d^{20} 1·085, α^{20}_{D} ($l = 0{\cdot}5$), −5·39°, $\alpha^{20}_{ye.}$ −5·60°, $\alpha^{20}_{gr.}$ −6·36°, $\alpha^{20}_{vi.}$ −13·33°, $[\alpha]^{20}_{D}$ −9·93°, $[\alpha]^{20}_{ye.}$ −10·32°, $[\alpha]^{20}_{gr.}$ −11·72°, $[\alpha]^{20}_{vi.}$ −24·57°.

d-*Glutamic Acid.*

Water; $p = 0{\cdot}99$.

t	d^t.	α^t_D ($l = 4$).	$\alpha^t_{gr.}$.	$[\alpha]^t_D$.	$[\alpha]^t_{gr.}$.
15°	1·004	+0·41°	+0·52°	+10·3°	+13·1°
40	0·995	0·32	0·43	8·1	10·9
51	0·992	0·29	0·40	7·4	10·2
60	0·998	0·27	0·37	6·9	9·5
*25**	—	—	—	*9·4*	*12·4*

* Interpolated.

$p = 1{\cdot}50$.

25°	1·003	0·66	0·80	11·0	13·3

$p = 2{\cdot}91$.

44°	1·002	1·20	1·44	10·3	12·3
64	0·994	1·00	1·25	8·6	10·8
75	0·990	0·90	1·15	7·8	10·0
25	—	—	—	*11·7*	*14·0*

Hydrochloric acid (N), 1·5 mols.; $p = 8{\cdot}752$.

t.	d^t.	α^t_D ($l = 2$).	$\alpha^t_{gr.}$.	$\alpha^t_{vi.}$.	$[\alpha]^t_D$.	$[\alpha]^t_{gr.}$.	$[\alpha]^t_{vi.}$.
13°	1·048	+5·81°	7·05°	15·60°	31·7°	38·4°	85·1°
32	1·042	5·50	6·72	14·65	30·2	36·8	80·3
43	1·037	5·32	6·53	14·10	29·3	36·0	77·7
25	—	—	—	—	*30·7*	*37·4*	*82·1*

Aqueous sodium hydroxide (1 mol.).

$p = 21{\cdot}2$, $[\alpha]^{25}_{gr.}$ $-0{\cdot}8°$; $p = 12{\cdot}25$, $[\alpha]^{25}_{gr.}$ $-3{\cdot}6°$; $p = 2{\cdot}86$, $[\alpha]^{25}_{gr.}$ $-6{\cdot}1°$.

Aqueous sodium hydroxide (2 mols.).

$p = 6{\cdot}56$, $[\alpha]^{25}_{gr.}$ $+11{\cdot}7°$; $p = 1{\cdot}44$, $[\alpha]^{25}_{gr.}$ $+10{\cdot}2°$; $[\alpha]^{40}_{gr.}$ $+8{\cdot}6°$.

The author's thanks are due to the Research Fund Committee of the Chemical Society for a grant towards the expense of this investigation, and to Dr. J. K. Wood for a supply of synthetic alanine from which the active benzoylalanine was prepared. The experimental portion of this work was performed at Birkbeck College, London.

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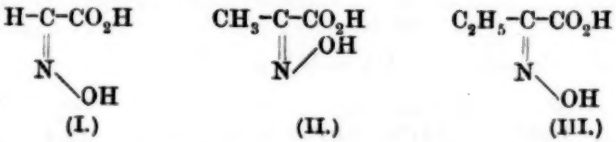
[*Received, March 25th*, 1918.]

XLV.—*The Dissociation Constants of some Higher Members of the α-Oximino-fatty Acids.*

By CEDRIC STANTON HICKS.

HANTZSCH and Miolati (*Zeitsch. physikal. Chem.*, 1892, **10**, 1), in an investigation of the dissociation constants of the lower members of the α-oximino-fatty acids, drew the conclusion that in the series $C_nH_{2n+1}\cdot C(:NOH)\cdot CO_2H$ as the series is ascended the dissociation constant diminishes in value, not steadily, but by a series of oscillations. Thus it was found that K for the first four acids, in which a hydrogen atom is successively displaced by the methyl, ethyl, and propyl groups, varied as follows: 0·0995, 0·0514, 0·0830, and 0·0685.

They considered that the variations were due to alternate fluctuations in the proximity of the hydroxyl to the carboxyl group, nearness of the hydroxyl, according to them, weakening the acid. This may be expressed graphically thus:



(I.) (II.) (III.)

As pointed out by Inglis and Knight (T., 1908, **93**, 1595), if the value for the second acid is abnormal, the series loses its interest,

and they accordingly began a reinvestigation of the conductivities of these acids.

In continuation of the work begun by these authors, an investigation of the dissociation constants of the higher members of the series has been undertaken.

EXPERIMENTAL.

The acids were prepared by Bouveault and Locquin's method (*Bull. Soc. chim.*, 1904, [iii], **31**, 1055) (compare Inglis and Knight, *loc. cit.*).

In the case of ethyl α-oximinohexoate, treatment with cold potassium hydroxide furnishes the potassium salt of the ester, the oximino-group thus acting as a negative group; when warmed with two molecular proportions of the alkali, the solution being acidified in the cold, the potassium salt (N·OK) separated, from which the acid was obtained on warming with hydrochloric acid.

Determination of Conductivities.

Owing to alterations in the laboratory being in progress at this time, it was impossible to prepare water with a smaller specific conductivity than $3{\cdot}3 \times 10^{-6}$.

The conductivity measurements were carried out at 25°, and owing in some cases to the rapid decomposition of the acids, together with the high conductivity of the water, measurements were not continued past a dilution of 256. All measurements except those at a dilution of 16 litres were duplicated. Since the conductivity was found to rise with the time, in order to obtain uniformity all measurements were made ten minutes after each successive dilution.

In the case of α-oximino-β-phenylpropionic acid, solution could only be effected by the aid of heat, even at a dilution of $N/32$. The solution, however, was evidently supersaturated, for after some hours crystals separated from it.

The values for Λ_∞ were calculated by means of Ostwald's empirical law, making use of the number of atoms in the molecule. The agreement between the values obtained in this way and those obtained from the sodium salt showed sufficient agreement in the case of the lower members to warrant the use of the same method for the higher members of the series (see Inglis and Knight, *loc. cit.*).

Equivalent Conductivities of the Acids.

α-Oximinoisovaleric Acid (m. p. 151·5°). $\Lambda_\infty = 378$.

$V =$	16	32	64	128	256
$\Lambda_v =$	48·15	66·5	87·5	110·8	136·8
$K =$	0·116	0·117	0·109	0·094	0·071

Mean value of K from the first three measurements = 0·114.

α-Oximino-n-*hexoic Acid* * (m. p. 131—132°. $\Lambda_\infty = 377$.

$V =$	32	64	128
$\Lambda_v =$	51·6	69·7	91·9
$K =$	0·0679	0·0656	0·0615

Mean $K = 0·0650$.

* The *ethyl* ester, $C_8H_{15}O_3N$, which has not been described, melts at 42°.

*α-Oximino*iso*hexoic Acid* (m. p. 150—151°). $\Lambda_\infty = 377$.

$V =$	16	32	64	128	256
$\Lambda_v =$	32·8	47·0	64·1	88·75	119·4
$K =$	0·0515	0·054	0·055	0·057	0·056

Mean $K = 0·056$.

α-Oximino-β-phenylpropionic Acid (m. p. 163°). $\Lambda_\infty = 377$.

$V =$	32	64	128	256
$\Lambda_v =$	49·5	67·7	89·7	118·7
$K =$	0·062	0·061	0·058	0·056

Mean $K = 0·57$.

α-Oximinophenylacetic Acid (m. p. 127°). $\Lambda_\infty = 379$.

Recalculated from Hantzsch and Miolati's results.

$V =$	16	32	64	128	256
$\Lambda_v =$	55·05	75·37	101·48	133·9	172·2
$K =$	0·1536	0·1545	0·1531	0·1508	0·1478

Mean $K = 0·1519$.

Stability of Acids in Aqueous Solution.

In order to obtain, if possible, some idea of the nature of the decomposition undergone by these acids in solution, an approximately $N/40$-solution of α-oximino*iso*valeric acid was placed in the thermostat at 25°. The strength of the acid was estimated at intervals by titration with $N/20$-sodium hydroxide.

The following are the values obtained, 5 c.c. of acid being employed for each titration:

Time in hours ...	0	2·5	3·5	5·5	21·5
Titre in c.c.	2·67	1·7	1·62	1·4	0·8

An attempt to determine the velocity constant for this decomposition was unsuccessful, owing probably to the doubtful nature of the products, of which carbon dioxide is one, but the concentration of which is uncertain. The result therefore only shows the diminution in strength approximately.

Discussion of Results.

Owing to the unstable nature of the higher members of this series of acids, little definite conclusion can be drawn.

The rise of conductivity with the time may mean a change from one isomeride into another, or it may simply mean a gradual decomposition, the conductivity ultimately becoming that of a complex solution.

It seems certain, however, that the oximinic hydroxyl group, rather than acting as an alcoholic group, as was implied by Hantzsch and Miolati, acts negatively, and so would lead to the greater strength of the "syn" acid, not the "anti" modification. There seems to be some anomalies in Hantzsch's conclusions as regards configuration, for (*Ber.*, 1891, **24**, 36) he states that the acetyl derivative of the α-oximinophenylacetic acid, melting at 145°, is decomposed by carbonate into the nitrile, carbon dioxide, etc., whilst that melting at 127° gives the original oxime. Since the melting point is a decomposition point, we should expect the "syn" acid to decompose more readily, that is, at the lower temperature. Again (*ibid.*), he states that the "syn" oxime is converted into the "anti" acetyl derivative by the process of acetylation, and since no mention of the preparation of the "syn" oxime is given, it is difficult to accept this as final.

Judging from the above results, and those obtained by Inglis and Knight, it seems, as was stated by these authors in connexion with the lower members, that the relation between configuration and dissociation constants is not so simple as was supposed, and an attempt to utilise the melting point as a means of assisting in the conclusion is just as unsatisfactory in its result.

One might expect to find some relation between the instability of the acids in aqueous solution and the configuration of their molecules; now in the case of α-oximino*iso*valeric acid, the strength diminished in twenty-one and a-half hours from 0·031*N* to 0·008*N*, whilst in the case of α-oximino*iso*hexoic acid, the strength only fell from 0·031*N* to 0·026*N* in twenty-four hours.

Here we have no simple relation in the change of titre, because, applying Bischoff's dynamic theory, the obvious conclusion would be that α-oximino*iso*hexoic acid would be the less stable of the

two, since the two methyl groups in the 5-position with respect to the hydroxyl of the oximino-group ought to force the hydroxyl and carboxyl groups nearer together and cause instability; but this is inconsistent with the fact that α-oximino*iso*hexoic acid is one of the easiest to prepare, and it is also fairly stable in aqueous solution, the titre falling off only slightly in twenty-four hours.

On the other hand, α-oximino*iso*hexoic acid may have the "anti" configuration, and this would be consistent with the fact that α-oximino*iso*valeric acid is much stronger than α-oximino*iso*hexoic acid. α-Oximinophenylacetic acid has a higher dissociation constant than α-oximino-β-phenylpropionic acid. This may be partly due to space relationships and partly due to the negative character of the phenyl group.

According to Bischoff and Hedenström (*Ber.*, 1902, **35**, 4096), it seems that, in general, the phenyl esters are hydrolysed with greater difficulty than the benzyl esters, thus pointing to hindrance due to the closeness of the nucleus; this same closeness would lead to proximity of oximino- and carboxyl groups, and thus to a stronger acid. As regards purely aliphatic acids, however, all that can be said at the present juncture is that there is strong evidence of the oximino-group reacting negatively, but that general conclusions as regards the series are unjustifiable.

My thanks are due to Dr. J. K. H. Inglis, at whose suggestion these experiments were carried out, for his guidance and assistance during the investigation.

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The Principles of Diffusion, their Analogies and Applications.

A Lecture delivered before the Chemical Society on June 6th, 1918.

By Horace T. Brown, LL.D., F.R.S.

How it comes about that one who is neither physicist nor mathematician should have the temerity to address you on the subject I have chosen for my lecture requires a few words of explanation.

I was perforce led to the study of the phenomena of diffusion some twenty years or so ago when investigating the photosynthetic processes which go on in the green organs of plants. A serious difficulty occurred in finding an explanation of the mode by which the assimilatory centres of a leaf can be supplied with the highly dilute carbon dioxide of the air with sufficient rapidity to account for the observed rate of increase of carbohydrates in a leaf lamina placed under favourable conditions of insolation.

Some idea of the required magnitude of this gaseous flow may be gathered from the fact that when a leaf is actively assimilating, it may happen that its surface is taking in atmospheric carbon dioxide more than half as fast as an equal area of a concentrated solution of alkali hydroxide would do if submitted to a constantly renewed current of air with the same carbon dioxide content.

This would be a surprising fact even if we regarded the whole surface of the leaf as being permeable to atmospheric carbon dioxide, but we now know with certainty that the leaf cuticle is impervious to carbon dioxide at partial pressures considerably above those at which it occurs in the air, and that the whole of the gaseous exchanges incident to assimilation take place by free diffusion through the stomata, minute apertures in the cuticle which only represent from about 1 to 3 per cent. of the total surface area of the leaf. Hence it follows that these minute openings must have the power of drinking in atmospheric carbon dioxide at a rate about fifty times greater than apertures of similar dimensions would do if they were filled completely with a constantly renewed solution of alkali hydroxide.

This led me to an experimental investigation of the laws of diffusion as applied to the passage of gases through small apertures and multiperforate septa, and ultimately to a complete explanation of the mode by which the diffusive flow can be accelerated by such structures as we find in the leaf, without postulating anything inconsistent with the well-established laws of diffusion; in fact, if

the exact conditions are defined, the degree of efficiency of such a mechanism can be deduced from those very laws.

It is to these and certain other cognate phenomena that I wish to direct your attention this evening, in the hope that my remarks may stimulate further inquiry into a subject of considerable interest, which has many applications in various directions.

That chemists generally in this country have paid far too little attention to diffusion phenomena, and to the important part which they play in many departments of chemistry and biology, is sufficiently evident from the scanty treatment which they have received in the majority of our text-books. This is the more remarkable and less excusable, since the very foundations of our knowledge of the subject were laid down by Thomas Graham, of pious memory, one of the founders and the first President of this Society. If chemists had rendered themselves more familiar with such questions, less surprise would have been expressed when Nernst, as recently as 1904, stated what ought to have been a self-evident proposition, that determinations of the velocities of reactions taking place at the boundaries of heterogeneous systems may be entirely vitiated if we fail to take into account diffusivity as a possible limiting factor.

In this connexion, I should like to refer as briefly as possible to some experiments which I made at the very outset of my inquiries, since they well illustrate this proposition of Nernst.

When a current of air containing any constant proportion of carbon dioxide up to about 18 or 20 parts per 10,000 is caused to move in a turbulent stream of known velocity over the free surface of a normal solution of sodium hydroxide, the temperature being maintained constant, the rate of absorption of carbon dioxide per unit area increases with the speed of the current until a linear velocity of about 260 metres per hour is reached. As long as the other conditions are unaltered, any further increase in the velocity of the air current is unattended by any change in the rate of absorption, the concentration of the carbon dioxide at the immediate boundary of the two surfaces having then attained its maximal value. Until this point is reached, gaseous diffusion is still playing some part in the reaction. That there is no corresponding limitation of the reaction in the liquid itself is shown by the fact that the rate of absorption is not influenced by any further stirring of the solution other than that produced by the air-current passing over it.

Under these conditions, the rate of absorption of the carbon dioxide per unit area of liquid surface varies directly with its partial pressure, and so exact is this relation that it has formed the

basis of a very accurate method for determining the amount of carbon dioxide in the air, which has the advantage that it is quite unnecessary to measure the volume of air employed.

The following table illustrates the degree of accuracy attainable by measuring the rate of absorption per unit area.

The first column shows the carbon dioxide content as given by passing measured volumes of air through a Reiset apparatus, whilst the second column gives the corresponding values deduced from the rate of surface absorption by a known area of the absorbent liquid over which unmeasured volumes of air have been passed in a turbulent stream at a sufficient velocity to produce the maximal effect. The results are given in parts per 10,000 of air reduced to normal temperature and pressure.

TABLE I.

(1).	(2).	Differences.
0·04	0·04	0
0·19	0·19	0
0·56	0·57	+0·01
1·08	1·08	0
1·15	1·21	+0·06
3·21	3·30	+0·09
3·36	3·30	−0·06
4·58	4·41	−0·17
4·89	4·93	+0·04
6·75	6·72	−0·03
7·65	7·50	−0·15
8·54	8·23	−0·31
12·53	12·40	−0·13
17·94	17·74	−0·20

The researches of Graham on the diffusion of gases, commenced in 1829, and continued at intervals up to 1863, are so well known that I need only make a passing allusion to them. They were carried out for the most part with an intervening septum of some porous material, such as plaster of Paris or thin plates of compressed graphite. When the gases communicated through such narrow channels or pipes he was led to a certain generalisation, which in his own words was as follows:

"The diffusion, or spontaneous intermixture of two gases in contact, is effected by an interchange in position of indefinitely minute volumes of the gases, which volumes are not necessarily of equal magnitude, being in the case of each gas inversely proportional to the square root of the density of that gas."

Such results had, of course, only relative values, and Graham clearly saw that absolute values could only be ascertained by allowing the gases to mix through a wide opening by free and unobstructed diffusion. It was only at a much later period that he

commenced any systematic experiments in this direction. He briefly described these in the concluding section of his paper of 1863 on the "Molecular mobility of gases" (*Phil. Trans.*, 1863, 385) with the sub-heading "Interdiffusion of gases without any intervening septum." Beyond showing that whilst a portion of carbon dioxide can diffuse through air at the rate of 7·3 cm. per minute, whilst a sensible portion of hydrogen travels in the same time about five times as far, these experiments did not lead to much, and the numerical results do not lend themselves to a determination of the coefficients of diffusion. Some seven or eight years afterwards, however, they served as a starting point for Loschmidt and his school in establishing a consistent theory of gaseous diffusion.

Long prior to this period Graham had been investigating the diffusion of liquids by his "open jar" method, and in his Bakerian Lecture of 1850 he described a large number of experiments on the comparative diffusivity of different substances in solution. His general conclusions were that, whilst every substance has its own particular velocity of diffusion, the actual rate of transference in solutions of the same substance depends on its initial concentration and on the temperature. Other things being equal, the amount of salt diffused in a given time is very nearly proportional to this initial concentration, and increases with the temperature.

Graham made no attempt to formulate any general law connecting the three variables time, concentration, and space traversed by the diffusate, but his observations fortunately attracted the attention of A. Fick, of Zurich, who, five years afterwards, in 1855, succeeded in developing from them a fundamental law for the operation of diffusion in a single element of space.

Fick's law of diffusion, like Ohm's law at an earlier date, was derived from the principles enunciated in 1822 by Fourier in his celebrated work on the Analytical Theory of Heat—principles which have been found applicable to so many diverse yet analogous sets of phenomena.

Lord Kelvin justly described this treatise of Fourier as a great mathematical poem. Although its beauty and magnificence can perhaps only be adequately and fully appreciated by the mathematician, it is a work of genius which cannot fail to excite the wonder and admiration even of those who, like myself, have not the requisite mathematical knowledge to follow it in all its details.

It was no doubt the ninth chapter of this treatise, dealing with the linear diffusion of heat in rigid substances, which gave Fick the desired clue to his law of diffusion.

Fourier had shown that if we imagine a plane lamina of conducting material with parallel faces, one of which is kept at a constant temperature ϑ_1, and the other at a lower temperature ϑ_2, and sufficient time has elapsed to establish a permanent flow of heat between the two surfaces, then the quantity of heat Q, flowing through the lamina in a given time t, will be directly proportional to the temperature difference $\vartheta_1 - \vartheta_2$ of its two surfaces. Q must also be directly proportional to A, the area of the lamina, and inversely proportional to its thickness x, so that we get the following general expression for the steady condition of the flow of heat:

$$Q = k\frac{\vartheta_1 - \vartheta_2}{x}At.$$

in which k is a quantity dependent on the nature of the substance and representing its conductivity. k is a constant if the conductivity does not vary with the temperature, and may be defined as numerically equal to the quantity of heat which will flow through unit area of a lamina of unit thickness in unit time, when there is unit difference of temperature between the two faces.

If the lamina is supposed to have an infinitely small thickness dx, and there is an infinitely small temperature difference between its two faces, the above expression becomes

$$Q = k\frac{d\vartheta}{dx}A \,.\, dt.$$

$\frac{d\vartheta}{dx}$ is the "gradient of temperature" at any point, so that the flow through unit area per unit time is numerically equal to the *conductivity* multiplied by the *temperature gradient*.

It is the particular merit of Fick that he was the first to express the idea that in all probability diffusion follows the same law, and that, *mutatis mutandis*, it is applicable to the transference of a solute in its solvent, just as Ohm had found it applicable to the flow of electricity in a conductor, the concentration of the solute being in one case the analogue of temperature and in the other of electrical potential.

Proceeding exactly according to the model of Fourier's mathematical development of a linear flow of heat, and assuming that in a diffusive column concentration gradient corresponds with temperature gradient, Fick arrived at the conclusion that when a solute diffuses in an axial direction along a column of constant cross-section, that is, one which is cylindrical or prismatic, the fall of concentration ρ, in any infinitely thin layer, at a distance x from

any point of reference in the column, should in a given time t satisfy the partial differential equation.

$$\frac{\delta\rho}{\delta t} = -k\frac{\delta^2\rho}{\delta x^2}.$$

In this formula k represents the coefficient of diffusivity which, subject to certain limitations, presently to be referred to, is constant for any given solute and solvent as long as the temperature does not vary. It is the exact analogue of Fourier's coefficient of heat conduction.

To quote Fick's own words: "According to this law, the transfer of salt and water occurring in a unit of time between two elements of space with differently concentrated solutions of the same salt must, *caeteris paribus*, be directly proportional to the difference of concentration, and inversely proportional to the distance of the elements from one another."

The law should hold good for any case of diffusion in which the lines of flux are parallel to each other, whether the condition of steady flow has been attained or not, but, owing to the difficulties attending the calculation of a sufficient number of values for the development of the integrals of the equation for special cases, Fick sought the requisite experimental proof in an examination of the distribution of density in a diffusive column which had attained the state of dynamic equilibrium. Under these conditions, the diffusive flux no longer alters the concentration in the space through which it passes, since each infinitely thin layer is receiving as much salt on one side as it is passing on to the next similar layer in juxtaposition.

The above fundamental equation can be shown to contain the proposition that when such a steady condition has been reached, the differences of concentration of any two pairs of strata in the column must be proportional to the distances of those strata, so that the decrease of concentration measured along the axis of the column ought to vary as the ordinates of a straight line.

The experimental method by which Fick attempted to verify this deduction was a somewhat crude one, but the results as a first approximation were found to be in fair accord with theory. Since his time many observers have introduced more refined processes for determining the progressive variations of concentration in a static column, based on optical, chemical, and electrical methods. By far the most satisfactory of these is due to Weber, who in 1879 made use of the fact that the *E.M.F.* developed between two electrodes of zinc or two of copper, immersed respectively in solutions of zinc sulphate and copper sulphate, can be used for measuring with great exactness the concentration at the boundary surface

in contact with the electrodes. The results in every way confirmed the accuracy of Fick's law.

Graham in his last paper on liquid diffusion, published in the *Philosophical Transactions* for 1861, recorded the results of a further series of experiments in which he used an improved method of 'jar-diffusion,' which enabled him to ascertain the degree of concentration of a salt in progressive layers of the diffusion column of a certain definite thickness. He does not refer to the important generalisation of Fick, which was apparently unknown to him, so that his conclusions as regards diffusion velocities are only of relative and qualitative importance. It was not until Stefan in 1879 had submitted these latest results of Graham to mathematical treatment that they were shown to be, on the whole, in accord with Fick's law. That the desired experimental verification should in the first place have been forthcoming from studies on hydro-diffusion rather than from those on gaseous diffusion is not surprising, since, in the latter instance, the molecular interpenetration, which is the essence of the process, takes place with far greater rapidity, and the difficulties in preventing mass movements are correspondingly increased.

Satisfactory proof that the progress of gaseous diffusion can also be expressed by Fick's law was first given by Loschmidt in 1870, the partial pressures of the interpenetrating gases being equivalent to the 'concentration' in hydro-diffusion. As might be expected, the law also holds good for the diffusion of vapours proceeding from the surfaces of volatile liquids.

A full and complete theory of gaseous diffusion from the kinetic point of view has still to be formulated, although so much has been done in this direction by mathematical physicists that there is a reasonable hope that all the observed phenomena will ultimately be deducible from a completed dynamic theory. Be that as it may, however, Fick's law or Fourier's law, whichever we may choose to call it, is one that enables us to solve nearly all the problems met with in practice, and it has the advantage that it is quite independent of any hypothetical assumptions as to the nature, constitution, or molecular condition of the substances taking part in diffusion, provided no dissociation occurs during the process. It merely gives in a compendious and useful mathematical form the experimental relations which exist between the three variables concentration, time, and space traversed in such a manner as to admit of ascertaining the state of the system at any given stage. Like the Phase Rule, it is a theorem which would still remain true even in the unlikely event of our present kinetic and molecular theories being radically modified or entirely abandoned.

The essence of Fick's law is that the 'driving forces' which cause the transference of a substance from regions of high to regions of low concentration are proportional to the concentration gradient.*

Fick's fundamental law, like all other "laws," has its limitations and must be regarded merely as a close approximation to the truth, and subject to correction as our knowledge increases. As it stands it may be compared with the uncorrected gas law of Boyle connecting pressure with volume. It assumes, for instance, that the coefficient of diffusion, k, at a given temperature is constant and independent of the concentration, which is certainly not strictly correct.

In his "Kinetic Theory of Gases," O. E. Mayer, in attempting to deduce the theoretical formula of gaseous diffusion from the kinetic considerations of Maxwell and Stefan, indicates that whilst the dynamical theory is in accordance with observation as far as the influence of temperature and pressure is concerned, his dynamic formula suggests that k, the diffusivity coefficient, ought to vary slightly with the number of molecules of one or the other kind of gas in unit volume of the mixture; that is to say, it ought to assume a somewhat different value in different parts of a diffusive column, dependent on the ratio of mixture.

Small progressive variations of this kind have been recently recorded by Jackmann, Deutsch, Schmidt, and Lonius for the free interdiffusion of various pairs of gases, but it is questionable whether the very small differences recorded are not within the limits of experimental error (see Jean's "Dynamical Theory of Gases," p. 334). Moreover, these experiments were necessarily conducted with the two gases initially at equal pressures, and therefore containing the same number of molecules per unit volume. O. E. Mayer has pointed out that these are not the best conditions for ascertaining if k varies with the ratio of mixture, and that we ought to employ gaseous mixtures containing only small masses of one of the constituents.

* It is somewhat surprising that the phenomena of osmotic pressure have not been often regarded from this point of view.

It is as legitimate to speak of the concentration of the *solvent* in a solution as the concentration of the *solute*, both are expressed by $\frac{\text{mass}}{\text{volume}}$. As the concentration of the solute increases that of the solvent diminishes. When a solution and the pure solvent are separated by a membrane impervious to the solute the inequality of "concentration" of the solvent on either side of the membrane must necessarily result in a diffusion current passing across the membrane from the region of high concentration of the solvent to regions of low concentration, that is, from the pure solvent to the solution. It is this process which gives rise to the "osmotic pressure."

During a certain stage of my work, I have been able to realise these conditions by determining the rate of the diffusive flow of atmospheric carbon dioxide, at a partial pressure of about 3/10,000 of an atmosphere, along a column of air after the static condition had been induced by introducing a perfect absorber of the carbon dioxide at one end of the tube.

If the coefficient of diffusivity for the system carbon dioxide–air is appreciably influenced by the ratio of mixture, these are just the conditions under which one would expect indications of it.

In these experiments, and in others made by determining the rate of flow through apertures of known dimensions, no positive evidence of any such differences was forthcoming (see Brown and Escombe, *Phil. Trans.*, 1900, [*B*], **193**, 241, 269).

In the phenomena of hydro-diffusion there is more convincing evidence that the value of k appreciably varies with the concentration, but until we have more accurate determinations of the coefficients of diffusivity of solutes than at present, this and other small disturbing influences, such, for instance, as those due to volume changes induced by the progressive dilution of the diffusate, cannot be evaluated with certainty.

Meanwhile, Fick's law is a very good approximation and sufficient for all ordinary purposes. It only requires correction in the same manner as does Fourier's law in the theory of heat-conduction: "as there the quantity of internal conduction slowly diminishes as the temperature rises, so here the quantity of the diffusion gradually sinks to smaller values as the concentration increases; Fick's hypothesis expresses the course of diffusion with only the same accuracy with which Fourier's elementary law represents the process of the conduction of heat in rigid bodies" (Weber).

I must now pass on to the consideration of some concrete examples of diffusion in certain typical and well-defined systems.

I have already referred to some of the conditions which exist in a diffusion column of cylindrical or prismatic shape when the concentrations of the diffusing substance are maintained at constant but unequal values at its two faces for a sufficient length of time to induce the steady condition of flow from one face to the other. In such a system, equal amounts of the diffusate must necessarily pass across each cross-section in equal intervals of time, and the fall of concentration of the diffusate will be uniform; that is to say, if the densities or concentrations are plotted against the corresponding distances of the cross-sections from the point of origin, the slope or gradient of density will be represented by a right line

the steepness of which is inversely proportional to the total length of the column.

If the concentration at one face is represented by ρ, that at the other face by ρ_1 some value which is less than ρ, and the length of the column by L, then at constant temperature the magnitude Q of the flux will vary directly as the gradient $\frac{\rho - \rho_1}{L}$. Q will also be directly proportional to the area of the cross-section of the column, to the coefficient of diffusivity k, and to the time t.

If consistent units are employed, the diffusive *efficiency* of the system will be represented by the equation

$$Q = k \frac{\rho - \rho'}{L} At.$$

In such a static system the stream lines of the flux will be represented by an infinite number of straight lines drawn parallel to the axis of the column. On the other hand, every cross-section of the column corresponds with a surface of equi-density of the diffusate to which the lines of flux are normal, and the uniformity of the gradient may be illustrated by drawing any number of lines representing these surfaces of equi-density at equal distances apart.

Although the essential elements of the system have their analogues in the conduction of heat in a bar which has attained the steady state, the parallelism of the two sets of phenomena is only complete if we imagine such a bar to possess no power of thermal emission from its surfaces.

On the other hand, the diffusive flow is strictly analogous to the steady flow of electricity along a conductor of uniform cross-section maintained at its two ends at a constant difference of potential $V - V_1$. In this case, the coefficient of diffusivity, k, corresponds with the electrical conductance, and the surfaces of equi-density with those of equi-potential.

Some time ago Professor Hele Shaw (*Phil. Trans.*, 1901, [*A*], **95**, 303), while investigating the stream lines of a moving viscous film, which is known to obey Fourier's law, discovered that two-dimensional cases of magnetic lines of force can be illustrated in a very beautiful manner by the flow of differently coloured viscous liquids under a constant head of pressure. In a diffusive field, it has not been found practicable up to the present to demonstrate the existence of the actual lines of flux, but, on the other hand, it is quite possible to render visible the surfaces of equi-density of a diffusate, and from these to deduce the shape of the stream lines which are everywhere orthogonal to those surfaces.

In the early days I obtained visual evidence of the shape and

relation of the zones of equi-density in various systems by the intermittent diffusion of solutions of sulphates and chromates into a gel of agar or gelatin to which had been added a little barium chloride. In this way, the surfaces of equal concentration are self-delineated by the progressive bands or zones of the insoluble barium salts precipitated within the gel (see Fig. 1). Latterly for this purpose I have availed myself of the Liesegang phenomena, whereby, under favourable conditions, two opposing diffusive streams of reacting substances can be made to produce in the gel a rhythmical series of zones and bands which follow the contours of surfaces of equi-density.

I have here some examples which show the position of these surfaces as they exist in cylindrical and prismatic diffusion columns.

In hydro-diffusion, most of the coefficients of diffusivity which appear in our tables of physical constants have been derived from the observed rate of flow in columns which have attained the steady condition to which I have referred. The values of k are generally expressed in centimetre-gram-day units, reference being made to the temperature and the concentration of the solution at the head of the column. Many of the recorded values are only approximations, and have to be treated accordingly. The static method is only rarely applicable to gases, but in a modified form I have shown that it can be successfully employed in determining the diffusivity of atmospheric carbon dioxide in the mixed gases of the air, although its partial pressure is so small.

We have seen that as long as we confine ourselves to the study of diffusive columns which have attained the steady condition of flow, the relations of the various factors which determine the rate of flow and the distribution of density in the column are capable of simple mathematical treatment. If, however, these conditions are not completely fulfilled, and the diffusate is still in process of extension into fresh regions of the column, the particular state of the system can no longer be determined by elementary mathematics, but nevertheless can be deduced from the fundamental equation of Fick when certain definite information is forthcoming as to the conditions of the experiment.

I have here a cylindrical column of agar gel down which is diffusing dilute hydrochloric acid, the concentration of which is maintained constant at the upper face of the column. To this gel has been previously added a little Congo red, and the degree of penetration of the acid is marked by the progressive change of colour from red to blue.

Since the acid diffusate is constantly advancing further and

further from its source, it is evident that any given stratum in the blue part of the column must be receiving more of the acid on its upper surface than it is transmitting from its lower surface to the next similar stratum immediately below it, so that the fall or gradient of density of the diffusate cannot be uniform, as it is in a diffusive column which has attained the static condition. A complete definition of the state of such a system at any desired moment is, however, derivable from the partial differential equation of Fick if we have some means of determining the exact position in the advancing column of a definite and thin stratum where the concentration of the diffusate has a known small value, and we can measure the distance between this stratum and the face of the column, where the acid is maintained at a known concentration.

The extreme limit of the blue coloration corresponds with such a definite stage, and the concentration at this point can be ascertained by a preliminary titration experiment. Knowing the length of the blue column, the ratio of the two concentrations, and the time the experiment has lasted, we have all the elements requisite for calculating the distribution of density in the column and the value of k.

I am indebted to Sir Joseph Larmor and to Mr. R. A. Fisher for a complete mathematical treatment of this problem, which is practically identical with that of a cooling Earth as investigated many years ago by Lord Kelvin. I need not trouble you with the equation which fits all the required conditions, and will only remark that the calculations are much facilitated by the fact that the equation involves the Probability Integrals of the Normal Curve of Errors, which has been thoroughly tabulated, and is much needed in the Theory of Gases.

One of the conclusions reached during the mathematical analysis is that if a succession of observations are made on such an advancing column of diffusion, the time t requisite for the extension of the blue coloration along the axis ought to be directly proportional to the square of the length x, measured from the free surface of the gel, so that $\frac{x}{\sqrt{t}}$ ought to be constant for all times. How closely this deduction accords with direct experiment will be noticed from the following results, obtained in the diffusion of dilute hydrochloric acid under the described conditions.

Time in hours. t.	Length of blue column. x.	$\frac{x}{\sqrt{t}}$.
1·0	8·0 mm.	8·00
3·0	14·0 ,,	8·08
5·5	19·0 ,,	8·10
7·41	22·0 ,,	8·08
18·0	34·0 ,,	8·01
*24·0	40·0 ,,	8·16

* By this or some similar method it is quite possible to determine how k, the coefficient of diffusivity, varies with the initial concentration of the solute at the face of the column.

So far, we have been considering systems in which the stream lines of the diffusive flux are parallel to each other and to the sides of a containing vessel which is cylindrical or prismatic in form. We have seen that in such cases, when the steady condition of flow has been attained, the gradient of density of the diffusate is uniform from end to end of the column, and that this uniformity of gradient can be illustrated by drawing at right angles to the axis, and at equal distances apart, a series of lines corresponding with the surfaces of equi-density. This uniformity of gradient no longer holds good, however, if the stream lines are rendered *convergent* or *divergent* by suitable means.

Suppose, for instance, we have a steady diffusive flow taking place along a tube having the form of a truncated cone. In those regions where the stream lines are more crowded together, that is to say, in the narrower part of the tube, the gradient of density is greater than it is in the wider part. If, therefore, we desire to illustrate this as we have done for the cylinder, we have to draw the lines corresponding with equal decrements or increments of density closer and closer together as the narrower end of the tube is approached.

For a given difference of "diffusion potential" between its two ends, the actual "efficiency" of a conical tube is calculable if we know the length of the truncated cone, its solid angle, and the particular value of k for the diffusing substance, but as this is only a special case deducible from diffusion around a sphere, which we shall presently consider, I will not dwell on it further except to compare the relative efficiency of a truncated cone and that of a cylindrical tube of the same length which has a uniform cross-section equal to that of the smaller end of the conical tube. This difference may be illustrated by a concrete example.

Suppose we have a truncated cone of 10 cm. in length, the smaller end of which has a spherical area of 1 sq. cm. at a distance of 1 cm. from the apex of the completed cone; then it can be shown that under similar conditions the diffusive flow ought to be *eleven* times greater through the conical tube than through a

cylindrical tube of the same length with a uniform cross-section equal to that of the smaller end of the conical tube.

Such accelerations of the diffusive flow through conical tubes can be readily verified experimentally in various ways. The principle is one which must have an important application in the respiratory organs of air-breathing animals, especially in the alveolar and higher regions of the lungs which lie beyond the influence of the tidal air, and in which the interchange of gases is dependent solely on diffusion.

When a body of spherical shape capable of acting as an absorber or an emitter of a diffusible substance is suspended in a field which is free from convection currents, the direction of the flux, to or from the sphere as the case may be, will be represented by a series of lines drawn radially from its centre, and the surfaces defining regions of equal density of the diffusate will form a series of external shells concentric with the sphere.

Let us first consider a sphere which is acting as an absorber in a practically infinite diffusive field in which the initial concentration has some fixed value represented by ρ, and that a sufficient time has elapsed to induce the steady condition of flow. We will also assume that the sphere is a perfect absorber, that is to say, that at its immediate surface the concentration of the diffusate is always maintained at zero. Under these conditions, the concentration of the diffusate around the sphere will vary from zero at its immediate surface to a value which is practically ρ in some region remote from the sphere.

Strictly speaking, ρ is a limiting value which theoretically is never reached, but for practical purposes it may be regarded as attained at distances exceeding ten diameters of the sphere, so that similar spheres at this distance apart would exercise very little interference with each other.

The distribution of the density or concentration of the diffusate around the sphere will be such that, proceeding from its surface outwards in a radial direction, the defect of density, represented by $-\rho$, will vary inversely with the radial distance from the centre of the sphere. Thus at radii 1, 2, 3, 4 . . . the negative densities will be represented by $-\rho$, $\frac{\rho}{2}$, $-\frac{\rho}{3}$, $-\frac{\rho}{4}$, . . ., whereas the actual positive densities, measured in the same direction, progress as 0, $\frac{1}{2}\rho$, $\frac{2}{3}\rho$, $\frac{3}{4}\rho$ . . .

At a distance of, say, 20 radii, the diffusate will consequently have a concentration of $\frac{19}{20}\rho$, or within 5 per cent. of the limiting value.

In a system such as this (the steady condition of flow being postulated), it is evident that during any given time interval equal amounts of the diffusate pass through each one of any number of concentric shells of equi-density described around the acting sphere. Since the surfaces of spheres are proportional to the square of their radii, this equality of flow implies that if we compare any two of the shells, the flow through unit area in each case must be inversely proportional to the squares of the radii. The flow per unit area is, however, directly proportional to the gradient of density, so that in such a field of diffusion as we are considering the gradient of density, that is to say, the fall of density per unit of radial length, must everywhere be inversely proportional to the square of the radius.

This leads to the conclusion that if we have two spheres of different dimensions acting as perfect absorbers in the same field of diffusion, and they are placed at such a distance apart as not to interfere with each other sensibly, then their relative *efficiencies*, as defined by the amount of diffusate which they will absorb in a given time, are not proportional to their surfaces, but to their linear dimensions. Thus a sphere of double or half the unit radius will absorb in a given time double or half the amount of diffusate.

If we represent the "efficiency" of an absorbing sphere by Q, its radius by r, the maximal concentration of the diffusate at some remote point by ρ, and the coefficient of diffusivity of the substance by k, we get the following general expression, which, *mutatis mutandis*, is also applicable to an emitting sphere when the steady condition is reached:

$$Q = 4\pi r \rho k.$$

If the sphere is not a perfect absorber and the diffusate has some ascertainable concentration at its surface, represented by ρ_1, then we should have to substitute $\rho - \rho_1$ for ρ in the above equation.

It will be noted that the phenomena of steady diffusion around a sphere are strictly analogous with those exhibited by a freely suspended and insulated spherical conductor which is electrically charged. The concentric shells of equal density of the diffusate correspond with the shells of equipotential in the dielectric surrounding the charged sphere, whereas the gradient of density measured along the lines of flux corresponds with the gradient of potential around the charged sphere measured along the lines of force. Moreover, what we have termed the 'efficiency' of the diffusive sphere is the exact analogue of the electrostatic *capacity*, both varying directly with the linear dimensions of the sphere.

If in spherical diffusion we describe a series of the concentric

shells of equal density at the appropriate intervals corresponding with equal increments or decrements of density, according to whether the sphere is absorbing or emitting, we obtain a figure which also represents the relative position of the equipotential zones around a charged sphere for equal differences of electrical potential, and in a gravitational field the relative position of the zones corresponding with equal differences of gravitational force.

Further striking and interesting analogies between the electrostatic and diffusive phenomena come to light if we study the lines of force and the equipotential surfaces around two spheres charged to the same electrical potential, and compare these with the surfaces of equi-density and the corresponding lines of diffusive flow induced in a diffusive field by two emitting spheres sufficiently close together to interfere with each other's action.

I will first show you the theoretical disposition of the surfaces of equipotential around two spheres charged to the same potential with electricity of a similar kind.

This illustration (Fig. 2) is taken from a drawing given by Clerk Maxwell in his "Electricity and Magnetism." For the sake of simplicity, I have omitted the actual lines of force, which in this two-dimensional projection would in all cases be normal to the equipotential lines. The forms taken by these lines or surfaces were the result of laborious calculation.

I will now show you (Fig. 3) how in the case of diffusion through two circular apertures the analogous surfaces of equi-density of the diffusate can be self-delineated by the interaction of the stream lines radiating from and to the apertures, thus giving a sectional representation of the shells of equi-density around spheres of corresponding diameters, set at similar distances apart in the same diffusive field. In the particular case shown on the screen, the interfering rings were produced by intermittent diffusion of alkaline sulphates and chromates into a gel containing a little barium chloride. Similar phenomena on a small scale can also be produced by the interference of two sets of Liesegang's rings formed by the diffusion of a solution of lead nitrate through two small apertures in a thin plate of celluloid floated on an agar gel containing a little potassium iodide. Examples of this are before you.

In such a system, however produced, the reacting substances travelling in opposite directions mark out regions of equal concentration of the diffusates, the true stream lines being orthogonal to these surfaces.

It will be noticed, in the first place, that in the early stages of their formation the rings lie closer together around the smaller than around the larger aperture, just as is the case with the zones

Fig. 1.

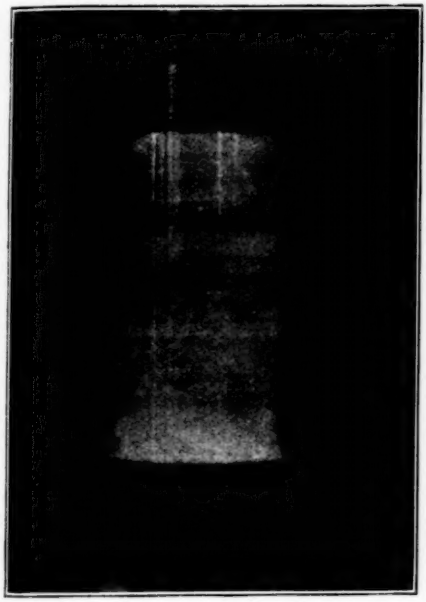

Fig. 2.

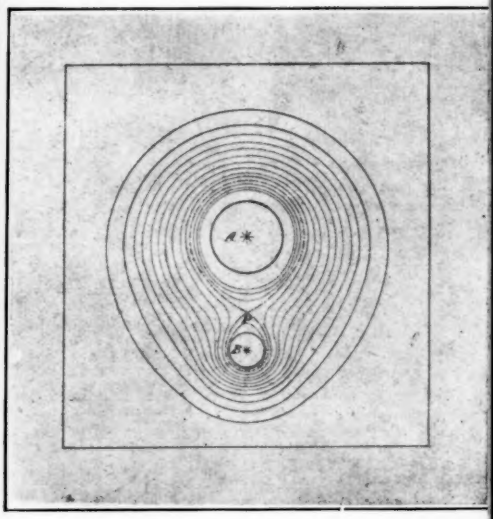

Fig. 3.

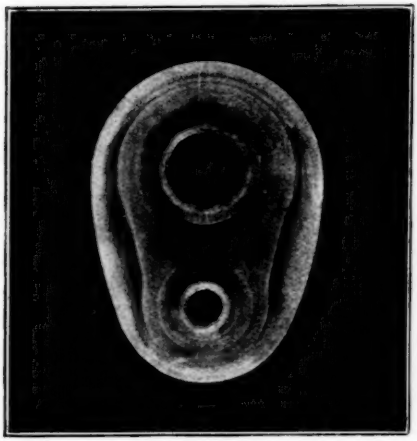

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FIG. 4.

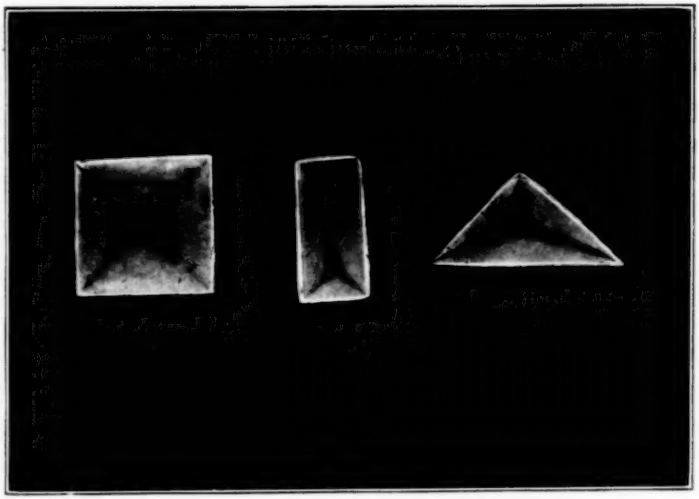


FIG. 5

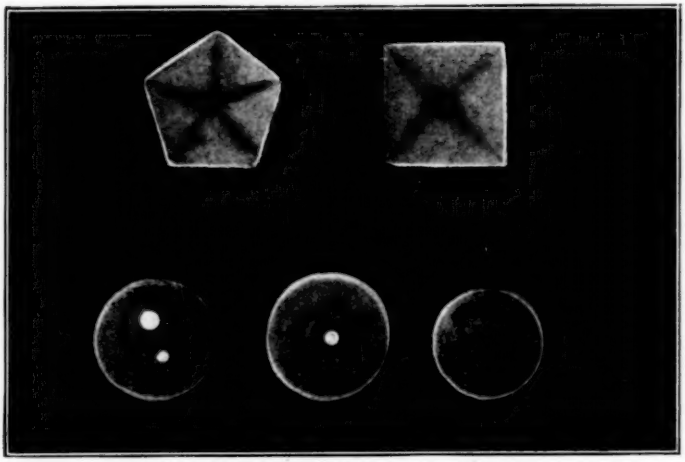


FIG. 6.

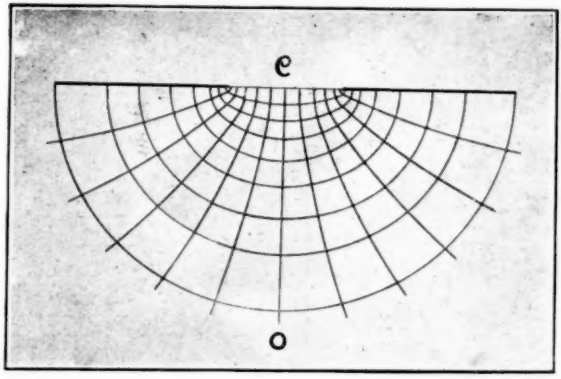


FIG. 7.

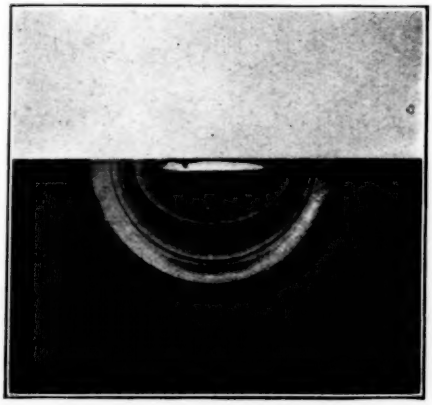


FIG. 8.

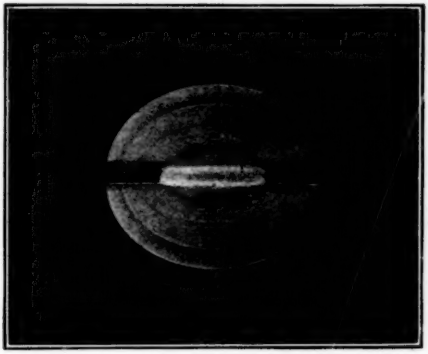


FIG. 9.

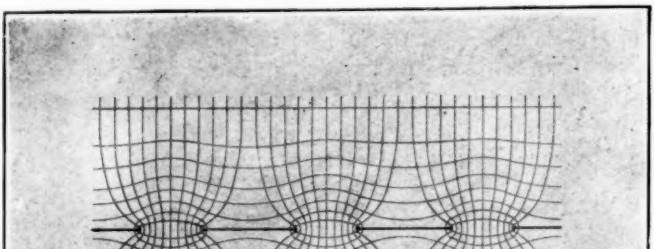


FIG. 10.

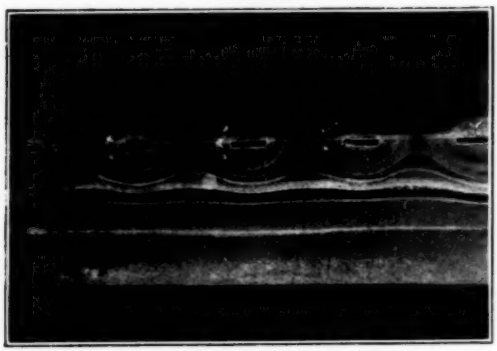
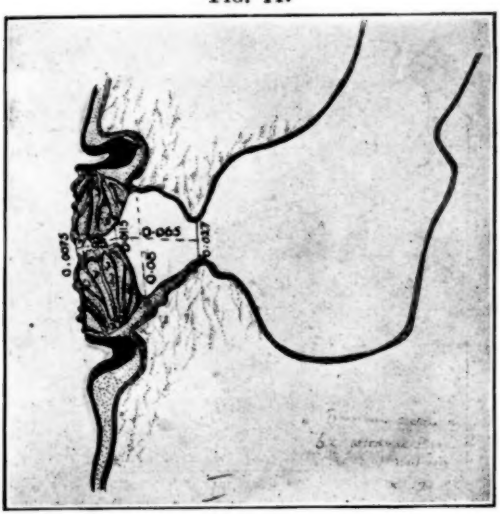


FIG. 11.



of equipotential around two spheres of unequal size electrically charged to the same potential.

As the divergent stream lines of diffusion progress, they begin to interfere with each other, and the rings to which they are normal begin to change their shape, ultimately fusing into a single system similar to the equipotential lines of Clerk Maxwell (see Fig. 2).

The diffusive and the electrostatic systems correspond in every detail. Maxwell by his laborious graphical method showed that if any one of the lines of the combined system is regarded as defining the surface of a single body (which in this case would have the shape of a dumb-bell with one end larger than the other), the equipotential surfaces come closer together at the smaller end, further apart at the larger end, where the curvature is less, and furthest apart of all in the centre of the dumb-bell, where the curvature is negative, the relative nearness of the lines indicating the relative density of the charge at these points.

You will see all this well exemplified in the analogous diffusive system. Where the surface curvature is greatest, there the equi-density lines lie closer together, thus indicating a higher gradient of density in these regions and a greater diffusive flow per unit area.

You will also observe, and perhaps this is the most interesting point of all, that Maxwell marks a certain region (*P*, Fig. 2) in the line joining the centres of the electrified spheres, which he states is a point of equilibrium, and that the surface density on a body of the form of this surface would be zero at this point.

This region of equilibrium is also defined in the diffusion figures of Fig. 3 as one of no precipitation; it is, as it were, a "dead spot."

If we fill a tube open at both ends with a gel containing a little barium chloride and then immerse it in dilute sulphuric acid, precipitation of barium sulphate progresses equally from either end of the tube until its centre is approached. There is, however, always a narrow central zone in the middle of the tube which remains clear, no matter what the terminal concentration of the acid may be or how long the experiment has lasted. The same thing occurs when the diffusion of the acid takes place centripetally from the edges of a circular glass cover-glass placed over a drop of the same gel placed on a glass slide, but in this case the dead space takes the form of a circular spot.

The explanation is that the two reacting substances, the sulphuric acid and the barium chloride, are diffusing in opposite directions, and that the barium ions have been depleted from the equilibrium zone before the acid reaches it, a fact which is readily demonstrated

by extruding the column of gel from the tube, dividing it in the centre of the 'dead' region, and applying a little sulphuric acid to the cut ends. When a diffusible coloured substance is employed in solution, the same phenomenon is observed at first, but ultimately, as might be expected, the column shows an equal distribution of colour throughout.

There is a further analogy to certain acoustic phenomena which is not without interest. The dead space in a tube such as I have described corresponds in position with that of the node of an open organ pipe when it is sounding its fundamental note. This analogy may be carried still further. If, for instance, inward diffusion takes place simultaneously from all the four edges of a square cover-glass, the four opposing streams of the reacting diffusates mark out the regions of equilibrium in the form of a regular cross with its arms directed towards the four corners of the square, thus producing an exact picture of the well-known Chladni's figure which marks out the nodes of a square vibrating plate bowed at the centre of one of its edges.

By varying the shape of the plate, a further instructive series of interference diffusion figures can be obtained, of which a few examples are given (see Figs. 4 and 5). On the table are further illustrations of somewhat similar figures produced by Liesegang rings of lead oxide. By suitable arrangement, it is possible to imitate the stratification of natural agates in this manner.

Before leaving the subject of spherical diffusion, I must dwell for a moment on the application of its principles to certain chemical and biological problems.

We have seen that in a diffusive field the actual "efficiency"* of a sphere, functioning as an absorber or emitter of the diffusate, varies directly with the radius of the sphere. Hence it follows that if a sphere is divided into any number of spheres n, of equal volume, and these are distributed in a similar field at such distances apart as not to interfere with each other, then the increased efficiency of the divided system will be represented by $n \cdot \sqrt[3]{\frac{1}{n}}$, when that of the original sphere is taken as unity. On the other hand, the increase in surface will only be represented by $\sqrt[3]{n}$, so that the 'efficiency' increases as the square of the surface.

For instance, if a sphere of unit volume is subdivided into 1000 equal spheres, the surface extension over that of the original sphere

* The 'efficiency' denotes the rate of emission or absorption for a unit or standard difference of concentration, and is analogous to the electrical capacity of a similar spherical conductor, that is, the charge held for unit difference of potential.

will be represented by 10, whilst the diffusive 'efficiency' of the whole subdivided system will be represented by 100.

The influence of a solid catalyst in increasing the velocity of a chemical reaction, such as that induced by a metal in the 'colloidal' state, is generally attributed to previous adsorption and condensation of the substrate on the surface of the particles.

Let us assume that the particles of the catalyst are spherical, and that the adsorption of the substrate at the boundary of the two phases has to attain a certain small value, which we will call the critical value, before the reaction starts, and, further, that the rate at which the chemical change takes place from this point is practically infinite.

Under these conditions, in order to maintain the rate of change appropriate to the concentration of the substrate in the main body of the liquid, we must retain the concentration at the surface of the particles at its critical value.

If these particles exceed a certain size, this will necessitate more or less vigorous stirring of the liquid. The smaller the particles become, however, the more nearly they will be able to maintain the critical concentration at their surface by diffusion alone, owing to the increasing convergence of the diffusive stream lines producing an ever increasing gradient of concentration. A point will ultimately be reached at which stirring will produce no increased effect.

It has often been assumed that the effect produced by subdivision of the catalyst under these conditions is directly proportional to the area of the surface, but it is evident that under appropriate conditions the activity of a unit mass of a catalyst must vary, not with the surface, but with the *square* of the surface.

These same principles enable us to understand how it is that minute dimensions confer advantages on certain micro-organisms in carrying out their life processes of nutrition and the correlated processes of fermentation and putrefaction.

When these organisms have little or no power of locomotion and the media in which they live have a low degree of mobility, they must be largely dependent on diffusion for the access of material from their surroundings and for the removal of the products of change from their immediate neighbourhood.

Minuteness of dimensions favours these convergent and divergent streams and enables the organism to supply its requirements from a medium of a much lower concentration of substrate than would be the case if the cell were of larger dimensions, thus exemplifying the "importance of being little"—and remaining so (see Slater and Sand, "The Rôle of Diffusion in Fermentation by Yeast Cells," T., 1910, **97**, 922).

Did time allow, I could give further examples of the applications of these same principles to diverse processes in which diffusion plays a more or less prominent part. They are, for instance, operative in the ignition of finely-divided pyrophoric substances, in the sparks produced by flint and steel, and in the rapid propagation of combustion of coal dust and other fine organic substances suspended in air.

We are too apt to regard diffusion as being necessarily a slow process, especially in liquids, which is by no means the case if the gradient of density is enhanced by the extreme convergence of the lines of flux on any particular point.

We have seen how the self-described diffusion figures surrounding two emitting spheres brought into each other's neighbourhood correspond in every detail with Clerk Maxwell's lines of equipotential and lines of force around two similar spheres charged to the same potential with the same kind of electricity.

The diffusion experiment may be so varied as to cause one of the circular perforations, corresponding with the sections of the spheres, to act as an emitter and the other as an absorber or 'sink' of the diffusate.

Under these conditions, the lines of equi-density of the diffusate tend to arrange themselves in accordance with Maxwell's figure of the equipotential lines around spheres, one of which is charged with positive and the other with negative electricity.

It is impossible to regard these analogous phenomena without suspecting that there is also a similarity in the dynamic relations of the two systems. We are, for instance, led to inquire whether in the case of diffusion there are any unbalanced forces which tend to move the bodies in a diffusive field.

I have recently referred this problem, which appears to present great difficulties, to Mr. R. A. Fisher, who is still at work on it. Whatever the final results of his analysis may be, it appears that if a small, elongated body which has a differential power of absorption at its two ends is introduced into a diffusive flow, it will tend to set itself along the lines of flux and to head up stream with its less absorptive end facing the region of the higher concentration of the diffusate.

If this deduction is correct, as I have but little doubt it is, it contains a physical explanation of certain phenomena of chemotaxis which have always been a great puzzle to the biologist. Let me give an example of what I mean.

The fertilisation of the non-motile egg-cells of the ferns and mosses is brought about by free-swimming, highly motile spermatozoids, which crowd into the archegonia in such a manner

as to suggest that there is some emission of an attractive substance from the opening which gives the needed directive force to the spermatozoids.

By immersing the free end of a fine capillary tube charged with a very dilute solution of sucrose into water containing the free-swimming spermatozoids of a moss, Pfeffer was able to demonstrate that whereas the movement of the spermatozoids in the body of the liquid occurred indifferently in all directions, it assumed a uni-directional character in the immediate neighbourhood of the orifice from which the sugar was diffusing, and the organisms crowded into the tube, which acted as a sort of artificial archegonium. Similar chemotactive movements also occur with the spermatozoids of ferns when the capillary is filled with an extremely dilute solution of malic acid. Under certain conditions, the movements are reversed in direction, when the chemotaxis is said to be *negative*. Somewhat similar movements have also been observed in certain motile bacteria, which are "attracted" to regions in which an evolution of oxygen is taking place within the cells of algæ containing chlorophyll and suitably illuminated.

Such movements, which at first sight appear to indicate a certain degree of intelligence on the part of the organisms, are, I believe, capable of a very simple physical explanation, which is at any rate worth serious consideration.

It must be borne in mind that in all such cases the real driving force of the spermatozoid or bacterium is supplied by its own motile organs, the flagella; all that we are called upon to explain is the origin of the *directive* force which is exercised when the organism finds itself in a suitable diffusive field in which the gradient of concentration of the diffusing substance is varying in a certain determinate direction.

Such a directive influence will certainly be exerted if the motile organism can act as an *absorber* of the diffusate, and this power of absorption is not uniform over its surface owing to a variation in the degree of permeability of the investing cell-membrane.

If those portions near the 'head' of the spermatozoid are less permeable to the diffusive substance than those nearer the flagellum in the rear, we should expect the organism to orientate itself in such a manner as to head towards the region of higher concentration—that is to say, towards the point of origin of the diffusive flow. This would correspond with the conditions of *positive* chemotactic movement. If, on the other hand, the region of the cell-membrane is more permeable at the front than at the rear, we should expect to get a heading down stream and a consequent re-

cession from the point of origin of the diffusate, that is, *negative* chemotaxis.

We have seen that when two perfectly absorbing spheres of different dimensions are suspended in the same diffusive field at a sufficient distance apart to exert no practical influence on each other, we should expect the ratio of their "efficiencies" as absorbers would be the same as the ratio of their electrostatic capacities when once the steady condition of diffusion has been induced. This should be equally true of bodies of any shape, so that if by experimental or other means both the electric capacity and volume of the body are known, we can by analogy determine its diffusive efficiency in a given field by referring it to that of a sphere of equal volume.

In the case of freely suspended spheres, the experimental verification of this proposition presents certain difficulties, which can, however, be avoided by a further simplification of the problem, as follows:

Clerk Maxwell has shown how it is possible to calculate the electric capacity of a planetary or oblate spheroid, which is formed by the revolution of an ellipse around its minor or polar axis, and to refer this capacity to that of a sphere of unit radius. Now a circular disk may be regarded as a particular and extreme case of a planetary ellipsoid in which the minor or polar axis has vanished. Such a disk if embedded flush in a non-conducting material has an electrostatic capacity of $\frac{1}{\frac{1}{2}\pi}$ times that of a sphere of the same radius. Hence, if the analogy really holds good, we should expect the "diffusive efficiency" of a disk to be represented by

$$\frac{4\pi kr\rho}{\frac{1}{2}\pi} = 8kr\rho,$$

if we count both sides of the disk, or $4kr\rho$ if the disk is absorbing or emitting on one side only.

We may substitute for such a disk a circular aperture in a very thin diaphragm through which diffusion is allowed to go on under well-defined conditions.

In these circumstances, by measuring the rate of flow of atmospheric carbon dioxide or of water vapour through circular apertures of known dimensions into a suitable vessel which ensures its absorption on the other side of the diaphragm, I have been able to obtain very complete evidence that experience and theory are in accord. Moreover, it is easy also to demonstrate that the rate of diffusive flow is directly proportional to the linear dimensions of

the aperture, not to its area. In fact, all the observed phenomena in their quantitative relations are strictly in accordance with those deducible from the application of the electrostatic analogy.

By using a method of this kind, it is quite possible in some cases to determine with considerable exactness coefficients of diffusivity, and it was in this manner that I was enabled to determine the value of k, the coefficient of interdiffusion of carbon dioxide and air, for dilutions of carbon dioxide representing about 3/10,000 of an atmosphere.

The conditions of evaporation in still air from a circular surface of liquid surrounded by a wide rim were mathematically investigated by Stefan in 1881, who also made use of the electrostatic analogy.

He concluded that the rate of evaporation in perfectly still air ought to be proportional to the linear dimensions of the liquid surface, and not, as was commonly supposed, to its area. Further, his analysis indicated that the divergent lines of flux of vapour emitted from the surface ought to be represented by a series of hyperbolas having their common foci in the bounding edge of the circular surface, whilst the curved surfaces of equal partial pressure of the vapour overlying the disk should form an orthogonal system of ellipsoids, also having their foci in the edge of the disk. Since these ellipsoids, conforming to surfaces of equal partial pressure, necessarily come closer together at the margin of the disk than towards its centre, Stefan concluded that, under the conditions postulated, evaporation proceeds more rapidly at the edge than at the centre.

Such a system is illustrated in a reversed position in Fig. 6, which also represents equally well the distribution of the lines of force and surfaces of equipotential in the neighbourhood of a circular electrified disk embedded flush in a wide, non-conducting rim.

I am not aware that Stefan or his successors ever attempted to verify his deductions by actual experiment. I am able this evening to show you how this can be done.

In the first attempts made by my colleague, Mr. F. Escombe, and myself, we used a rectangular glass cell divided horizontally by a plate of celluloid having a circular hole punched through it. The lower half of the cell was completely filled with a gelatin gel containing a little barium chloride, and the upper half with a solution of alkaline sulphate. The opposing streams of the reacting diffusates produced in the gel in the neighbourhood of the aperture an opaque spheroidal figure which changed its shape as it became larger. By photographing this at intervals and super-

imposing the negatives, it was seen that the limiting surfaces of the constantly changing figure marked out by the precipitation of the barium sulphate conformed exactly to the system of ellipsoids demanded by theory.

The process was further improved by the intermittent diffusion of sulphates and chromates through the aperture, thus forming a banded structure in the gel, well seen when the block of gelatin was divided by a vertical section. This further led to employing a semicircular aperture with its flat side coincident with the plane of one of the sides of the glass vessel, so that the arrangement of the banded structure on the diffusion spheroids was visible in cross-section through the glass. Further developments led to the use of narrow slits cut in a thin plate of celluloid which formed one side of a thin, rectangular cell filled with the gelatin–barium mixture. Such a slit manifestly corresponds with a vertical central section of a circular disk looked at edgeways.

In the slides now before you (Figs. 7 and 8) you have a photographic reproduction of such a system of the shells of equi-density in the immediate neighbourhood of the opening through which the diffusion is taking place. It will be noted that their shape and disposition are exactly those predicted by Stefan, the alternate zones of barium sulphate and chromate forming a series of confocal ellipsoids having their foci in the edges of the disk, and therefore approximating more and more to the spherical shape as we progress outwards. It is also to be observed that the ellipsoidal shells come closer together at the edges than in the centre, indicating that in these regions the gradient of density is greater, and consequently that the flow per unit area is also greater.

It must not, however, be supposed, as I have sometimes seen it stated, that the acceleration of diffusive flow produced by small apertures is dependent merely on this increased flow at the edges. There would be almost the same amount of acceleration if the equi-density zones could be imagined to be spherical instead of ellipsoidal. The acceleration of flow per unit area as the size of the aperture is diminished is conditioned in the main by the degree of convergence or of divergence of the lines of flux. The smaller the aperture, the greater becomes this convergence and divergence, with a corresponding increase in the gradient of density in its immediate neighbourhood.

The experimental study of diffusion through single apertures naturally leads up to a consideration of the effects to be expected from a series of small apertures in a thin diaphragm when such a multi-perforate septum is inserted in a line of diffusive flow.

One would expect, from what has been said, that if the apertures are small and arranged at suitable distances apart, the accelerated flow induced by each individual aperture would to a large extent neutralise the effect of the obstruction produced by the imperforate parts of the diaphragm, and that under favourable conditions the intervention of such a septum would not sensibly diminish the rate of flow in the diffusive column, although the aggregate area of the openings might be small as compared with the cross-section of the column.

This was actually found to be the case. As an instance, I may mention an experiment in which a thin film of celluloid perforated with 100 circular apertures per sq. cm., each one of a radius of 0·19 mm., produced no sensible effect in obstructing the static diffusion of atmospheric carbon dioxide down a column of air, although the imperforate parts of the septum blocked out nearly 90 per cent. of the cross-section of the column.

Just as the electric capacity of a plate is not considerably affected by cutting parts of it away and leaving an open framework, so also it is possible to block out a considerable portion of the cross-section of a diffusive column without materially altering the general static conditions on which the flow depends. In such a case, what I have termed the *diffusive efficiency* of the system is but little affected.

I have here a demonstration of this principle in these two columns of gel into which a dye has been diffusing for some time. In one case the column is entirely unobstructed, whereas in the other such a perforated septum as I have described has been inserted in the line of flow, thus cutting off about 90 per cent. of its effective area. You will notice that the efficiency of the column has not been sensibly reduced in the latter case.

In the accompanying illustration (Fig. 9), I have attempted to illustrate in diagrammatic form the manner in which the parallel lines of flux in a diffusive column are modified by the interposition of such a perforated septum. It will be noted that as the stream lines approach the apertures they become convergent and gradually assume parallelism again on the other side, since the lines of flux, like lines of force, cannot intersect each other.

On the other hand, there is an increased gradient of density in the immediate neighbourhood of the apertures, as evidenced by the zones of equi-density coming closer together in this region, and producing a more rapid flow through the septum.

That such a theoretical system conforms to the actual facts is shown by the succeeding illustration (Fig. 10), which shows a photograph of the zones of equi-density under these conditions produced

by intermittent diffusion of two reacting substances through a series of apertures.

In this principle resides the long-sought explanation of the effectiveness of the stomata of a green leaf in accelerating the interchanges of gases and water vapour which are requisite for the requirements of the plant.

From the dimensions and mode of distribution of these stomata, it is quite possible to calculate what their maximum diffusive efficiency ought to be under given conditions, both for carbon dioxide and water vapour, and to compare this with the actual interchanges as determined by experiment.

In all such cases as have been examined the theoretical efficiency of the mechanism, regarded merely as a piece of physical apparatus, is far in excess of any demands which could be made upon it. Whatever limiting factors may exist in the co-ordinated processes attendant on carbohydrate assimilation by a green leaf, whether of a physical or chemical nature, we cannot attribute any of them to faulty construction in the diffusive mechanism itself.

It is certainly extremely improbable that the green leaf is the only case in nature in which there has been a more or less perfect adaptation to these laws of diffusion through small apertures. It is true that up to the present it is the only instance in which a complete and satisfactory demonstration has been forthcoming of this remarkable adjustment of structure to function, but doubtless there exist many other examples of equal interest and importance which await further discovery. It is impossible, for instance, to observe the minute perforations in the closing membranes of certain vegetable cells without recognising how eminently suited these structures are for producing all the diffusive phenomena which belong to multi-perforate septa, and how admirably they are adapted, without any sacrifice of protective strength, to enhancing the rate of diffusive flow through the cell membrane separating contiguous cells.

Nor are these suggestive facts by any means confined to the Vegetable Kingdom.

It is many years ago since Graham hazarded the opinion that when insects are at rest and exerting no muscular effort of any kind, their respiratory processes are carried on entirely by diffusion along the ramifying tracheæ which communicate with the outer air through the stigmatic openings in the body segments.

The accuracy of this guess is rendered still more probable when we examine the structure of these stigmatic openings more closely.

I am indebted to Mrs. Cuthbert Baines for a beautiful microscopical drawing of the stigma of a caterpillar in medial cross-

section, from which you will see that the apparatus has in certain respects such a remarkable resemblance to the stoma of a leaf that it is impossible to avoid the conclusion that the gaseous exchanges of respiration in the insect are in a measure determined by this particular structure (see Fig. 11).

To elaborate and give the necessary proof of many of the statements I have made this evening would require, not one, but many lectures. The present summary, imperfect and discursive as it may appear, may nevertheless suffice to show that much may be expected from a continued study of diffusion and the application of its principles in various branches of science. One of the greatest pleasures of which the human mind is capable is engendered by this linking together of diverse sets of phenomena by some underlying common principle which is not at first recognisable. How well was this expressed nearly two thousand years ago by one who was both a great poet and a keen observer of nature—one who found his best solace and inspiration in the study of his forests, his flocks and herds, his vineyards, his corn lands and his hives!

"Felix qui potuit rerum cognoscere causas."

XLVI.—*Some Piperylhydrazones.*

By Albert Weinhagen.

The piperylhydrazine employed in this investigation was prepared by reducing nitrosopiperidine (Knorr, *Annalen*, 1883, **221**, 304). Unless otherwise stated, the condensations were effected according to the usual method of heating the aldehydes with the requisite amount of piperylhydrazine in alcoholic solution faintly acidified with acetic acid. As described in each instance, the products were then purified by such methods as proved most suitable.

Piperonalpiperylhydrazone.—This crystallises from alcohol in colourless needles melting at 65—67°. The hydrazone is readily soluble in ether, chloroform, benzene, or hot alcohol, less readily so in cold alcohol, and practically insoluble in water:

0·1916 gave 21·1 c.c. N_2 at 17° and 722 mm. N = 12·31.

$C_{13}H_{16}O_2N_2$ requires N = 12·07 per cent.

Salicylaldehydepiperylhydrazone.—This compound crystallises from alcohol in needles, at times in small rhombic plates, and

occasionally in octahedra, which interlace in such a manner as to form long, needle-like, prismatic structures. The compound melts at 71—72°, and is readily soluble in ether, chloroform, benzene, or hot alcohol, less readily so in cold alcohol, and practically insoluble in water:

0·1965 gave 24·7 c.c. N_2 at 17° and 711 mm. N = 13·84.
$C_{12}H_{16}ON_2$ requires N = 13·74 per cent.

Formaldehydepiperylhydrazone.—This crystallises from alcohol in prismatic needles melting at 78—79°. It is readily soluble in chloroform, hot light petroleum, or hot alcohol, less readily so in cold light petroleum or cold alcohol, and practically insoluble in water:

0·1270 gave 28·3 c.c. N_2 at 16° and 728 mm. N = 25·21.
$C_6H_{12}N_2$ requires N = 25·21 per cent.

Benzaldehydepiperylhydrazone.—This hydrazone crystallises from alcohol in small, five- or six-sided plates. The pure compound (which was analysed) melted at 68—69° (Knorr, *loc. cit.*, gives 62—63°, and Forster, T., 1915, **107**, 267, gives 68°).

Anisaldehydepiperylhydrazone.—Three grams of anisaldehyde were heated on the water-bath with 2 grams of piperylhydrazine and 2 grams of 50 per cent. acetic acid. The mixture soon became red, and ultimately an intensely reddish-violet syrup separated, which became crystalline on evaporating to dryness and allowing to remain for some time. By means of light petroleum, the hydrazone can be extracted from this mixture free from the red colouring matter, for the latter, whilst being readily soluble in alcohol, is quite insoluble in the former solvent. On evaporating the light petroleum, the hydrazone was obtained in small, colourless, hexagonal plates. The hydrazone obtained in this way possessed the property of turning reddish-violet when exposed to light, which was evidently due to traces of impurities. This ceased to be the case after it had been recrystallised from alcohol several times. The melting point ultimately remained constant at 54°. The hydrazone is readily soluble in ether, chloroform, light petroleum, or hot alcohol, less readily so in cold alcohol, and practically insoluble in water:

0·1897 gave 21·8 c.c. N_2 at 16° and 728 mm. N = 12·79.
$C_{13}H_{18}ON_2$ requires N = 12·85 per cent.

An attempt was made to avoid the formation of the reddish-violet colouring matter by condensing in alcoholic solution, but the results were precisely the same as before.

p-Hydroxybenzaldehydepiperylhydrazone. — This compound

separated from an alcoholic solution of 3 grams of piperylhydrazine, 4·5 grams of *p*-hydroxybenzaldehyde, and acetic acid, which had remained at the ordinary temperature for several days, whereas if the mixture is heated, a much inferior yield, accompanied by resinous red by-products, is obtained. The hydrazone is soluble in ether, chloroform, or hot alcohol. When recrystallised from the latter solvent, it melts at 161°:

0·1799 gave 22·7 c.c. N_2 at 18° and 726 mm. N = 13·91.

$C_{12}H_{16}ON_2$ requires N = 13·74 per cent.

p-*Aminoacetophenonepiperylhydrazone.*—Three grams of *p*-aminoacetophenone dissolved in alcohol were heated on the water-bath with 2 grams of piperylhydrazine and 2 grams of 50 per cent. acetic acid. The solution soon became yellow, and on cooling the mixture and allowing it to remain, no hydrazone separated. The mixture was accordingly evaporated to dryness. The brown, syrupy substance obtained in this way was practically insoluble in light petroleum, but treatment with this solvent converted it into a granular, faintly yellow mass, which was recrystallised from 95 per cent. alcohol several times. The pure white hydrazone obtained in this way crystallises in small prisms and prismatic needles melting at 108°. It is readily soluble in ether or hot alcohol, less readily so in cold alcohol, very sparingly so in light petroleum, and practically insoluble in water:

0·1468 gave 0·0110 H_2O at 110°. H_2O = 7·49.

0·1889 ,, 30·4 c.c. N_2 at 16° and 728 mm. N = 17·90.

$C_{13}H_{19}N_3,H_2O$ requires H_2O = 7·66; N = 17·89 per cent.

Hot dilute hydrochloric acid readily resolves this hydrazone into its components, of which *p*-aminoacetophenone was isolated and recognised by means of its platinichloride (Found: Pt = 28·78. Calc.: Pt = 28·69 per cent.).

Attempts to prepare the piperylhydrazones of propionaldehyde, acetone, *p*-aminobenzaldehyde, dextrose, galactose, and *l*-xylose gave rise to resinous red and brown products, whereas *iso*valeraldehyde furnished very small yields of a compound melting at approximately 122°, which was not analysed.

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XLVII.—*Acetyl*-p-*diazoimides derived from Substituted p-Phenylenediamines.*

By Gilbert T. Morgan and David Alexander Cleage.

Recent experiments on the diazotisation of acyl-*p*-phenylenediamines carried out with nitrous anhydride in dry solvents have led to the isolation of the simpler acyl-*p*-phenylenediazoimides containing respectively formyl, acetyl, and benzoyl groups (Upton and Morgan, T., 1917, **111**, 187). These results have since been confirmed by Dimroth and Leichtlin (*Ber.*, 1917, **50**, 1539), who have prepared benzoyl-*p*-phenylenediazoimide in aqueous solutions by the action of sodium hydroxide on benzoylaminonaphthalene-4-diazonium chloride.

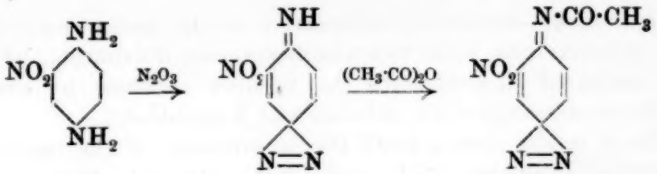
Researches extending over many years have shown that the formation of acyl-*p*-diazoimides from aromatic acyl-*p*-diamines is a general reaction which has been realised in a very large number of instances (T., 1905, **87**, 73, 921, 1302; 1906, **89**, 4, 1158, 1289; 1907, **91**, 1505, 1512; 1908, **93**, 602, 614; 1910, **97**, 48; *Ber.*, 1902, **35**, 888; 1906, **39**, 2869).

These results indicate that the presence of the acyl group doubtless plays an important part in the internal condensation leading to the production of acyl-*p*-diazoimides, yet there is a possibility that under suitable experimental conditions it might be possible to isolate the parent substances of this series of diazo-derivatives in which the acyl radicle is replaced by hydrogen.

With this object in view, the experiments recorded in the experimental section have been made on derivatives of *p*-phenylenediamine containing acidic substituents in the nucleus.

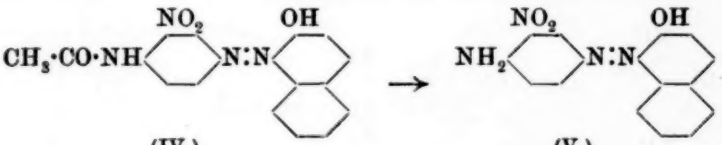
The difficulty of diazotising both amino-groups simultaneously in *p*-phenylenediamine is greatly increased when a nitro-group is introduced into the ring. Nitro-*p*-phenylenediamine (I) is accordingly a suitable base for the attempt to isolate a diazoimine produced by the diazotisation of only one of the amino-groups.

When this experiment is carried out with nitrous anhydride in well-cooled anhydrous solvents, an unstable, brown substance having the properties of a diazoimine (II) is produced. This product, however, becomes resinous when warmed to the ordinary temperature; it is stable only in a freezing mixture. While suspended in a cooled mixture of ether and acetone, this diazoimine can, however, be stabilised by acetylation with acetic anhydride, when 4-*acetyl*-3-*nitro*-p-*phenylene*-1-*diazo*-4-*imide* (III) is obtained:



(I.) (II.) (III.)

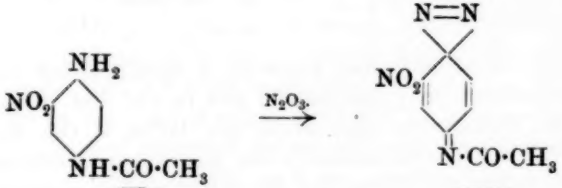
The constitution of this acetyl derivative, and hence that of the unstable diazoimine, are confirmed by the following series of reactions. The acyl-*p*-diazoimide is combined with β-naphthol to form the azo-derivative (IV), and this compound is hydrolysed to the



(IV.) (V.)

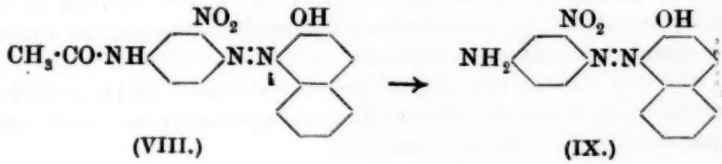
corresponding aminoazo-derivative (V). The latter product when diazotised and boiled with alcohol is converted into *m*-nitrobenzene-azo-β-naphthol, which is identified by direct comparison with the preparation obtained by combining diazotised *m*-nitroaniline and β-naphthol.

Further confirmation of this constitution for 4-acetyl-3-nitrophenylene-1-diazo-4-imide is obtained by preparing its isomeride, *4-acetyl-2-nitro-*p*-phenylene-1-diazo-4-imide* (VII). This diazoimide, obtained in a similar manner by diazotising 4-acetyl-2-nitro-*p*-phenylenediamine (VI) with nitrous anhydride in dry acetone,



(VI.) (VII.)

combines with β-naphthol to yield an azo-derivative (VIII), which on hydrolysis gives rise to an aminoazo-compound (IX). From

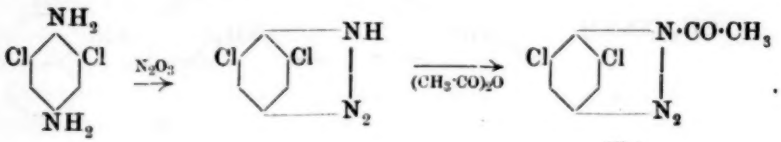


(VIII.) (IX.)

this aminoazo-derivative, elimination of the amino-group through the diazo-reaction leads to *o*-nitrobenzeneazo-β-naphthol, which can be compared directly with the product obtained by combining *o*-nitrobenzenediazonium chloride and β-naphthol.

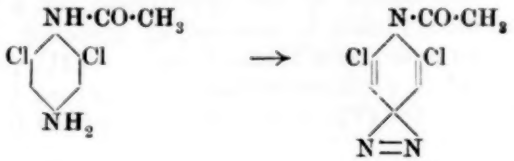
These results demonstrate the constitution of the two isomeric acetyl-*p*-diazoimides (III and VII) derived from 2-nitro-4-phenylenediamine, the former of which is obtained by acetylating the diazoimine of this diamine.

Similar results have been obtained in the case of 2:6-dichloro-4-phenylenediamine. This base on treatment with nitrous anhydride in well-cooled acetone yields an unstable diazoimine which can be stabilised by acetylation:



(X.)

The product (X), a grey, crystalline powder, combined readily with the naphthols and naphthylamines, giving colour reactions identical with those obtained from the diazoimide (XI) prepared by diazotising 1-acetyl-2:6-dichloro-*p*-phenylenediamine:

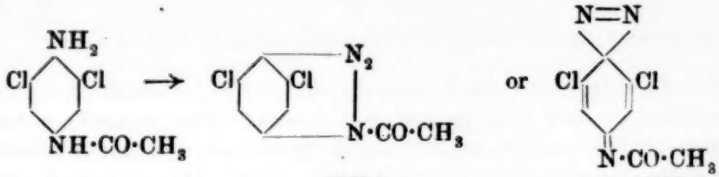


(XI.)

The latter diazoimide has, however, a bright yellow colour. The colour differences may possibly be due to the first compound being the cyclic diazoimide (X), whilst the latter is the diazoquinone-imide (XI). Or, alternatively, the less coloured compound might be a diazonium derivative and the other a diazo-compound. These differences, however, disappear on combining with phenols or reactive bases both forms of *acetyl*-3:5-*dichloro*-p-*phenylene*-1-*diazo*-4-*imide* giving the same azo-derivatives.

The alternative formulations (XII or XII*a*) for the product of acetylation of 2:6-dichloro-*p*-phenylenediamine is excluded by direct experimental evidence.

Acetyl-2:6-*dichloro*-p-*phenylene*-1-*diazo*-4-*imide* (XII) is prepared by treating 4-acetyl-2:6-dichloro-*p*-phenylenediamine with nitrous anhydride under similar conditions:



(XII.) (XIIa.)

The product, which is stable at the ordinary temperature, is almost colourless, thus suggesting the diazoimide configuration (XII) rather than that of the diazoquinoneimide (XII*a*). It combines readily with the naphthols and naphthylamines, giving colour indications differing from those of the two forms of acetyl-3:5-dichloro-*p*-phenylene-1-diazo-4-imide.

Experimental.

4-*Acetyl*-2-*nitro*-p-*phenylene*-1-*diazo*-4-*imide* (VII).

p-Phenylenediamine was acetylated by adding acetic anhydride (1·3 parts) to its 40 per cent. aqueous solution. The diacetyl derivative when nitrated either in glacial acetic acid or in concentrated sulphuric acid (compare *Ber.*, 1897, **30**, 980) gave its own weight of diacetyl-2-nitro-*p*-phenylenediamine. This product was half hydrolysed to 4-acetyl-2-nitro-*p*-phenylenediamine by boiling for fifteen minutes with 2 parts of crystallised barium hydroxide and 3 parts of water, the barium being then removed by passing carbon dioxide into the boiling solution. The filtrate on cooling deposited bulky, orange-red plates melting at 188°.

4-Acetyl-2-nitro-*p*-phenylenediamine (1 part) dissolved in 100 parts of pure dehydrated acetone was treated slowly with 5 c.c. of a 10 per cent. acetone solution of nitrous anhydride free from nitrogen peroxide, both solutions being cooled to −15°. The colour of the solution of the base changed from red to pale straw-yellow, and on the addition of an equal volume of pure dry ether the product separated in yellow plates, and was washed with anhydrous ether and dried in a vacuum desiccator in the dark:

0·1000 gave 22·5 c.c. N_2 (moist) at 9° and 770·8 mm. N = 27·31.

$C_8H_6O_3N_4$ requires N = 27·18 per cent.

4-*Acetyl*-2-*nitro*-p-*phenylene*-1-*diazo*-4-*imide* decomposed explosively at 142°. It darkened on exposure to light, and combined readily with β-naphthol when the two reagents were ground together.

Constitution of Acetyl-2-nitro-p-phenylene-1-diazo-4-imide.

Acetyl-2-nitrophenylene-1-diazo-4-imide was combined with β-naphthol (1 mol.) in glacial acetic acid. The product, a red azo-β-naphthol, melted at 298°, and developed a magenta coloration with concentrated sulphuric acid. When the saturated solution of this azo-derivative in glacial acetic acid was diluted with three volumes of water and warmed with excess of concentrated ammonia, the acetyl group was removed by hydrolysis. The resulting 2-nitro-4-aminobenzeneazo-β-naphthol was dissolved in absolute alcohol and treated with nitrous anhydride and a few drops of concentrated sulphuric acid at −10° to −15°. This diazonium solution combined with alkaline β-naphthol to a dark red bisazo-compound, giving an orange coloration with concentrated sulphuric acid. Another portion of the alcoholic diazonium solution was boiled gently, when nitrogen was evolved. The dark red powder left on evaporating the alcoholic solution was crystallised from 80 per cent. alcohol containing animal charcoal. It then melted at 206° and gave a reddish-violet coloration with concentrated sulphuric acid. A specimen of 2-nitrobenzeneazo-β-naphthol was prepared for comparison from β-naphthol and diazotised *o*-nitroaniline; it was a brownish-red to dark red powder melting at 209° and giving a violet coloration with concentrated sulphuric acid. The melting point of a mixture of the two preparations varied from 203° to 205°. In this way, the orientation of the nitro-group with respect to the diazo-group was ascertained and the constitution of the acetyl-diazoimide determined. 4-*Acetyl*-2-*nitro*-p-*phenylene*-1-*diazo*-4-*imide* gave the following colour reactions on conversion into its azo-derivatives, this combination being effected in pyridine:

Azo-derivative with:	Colour of the azo-derivatives.	Coloration with concentrated sulphuric acid.
β-Naphthol	Scarlet	Magenta
β-Naphthylamine	Red	Brownish-red
α-Naphthol	Scarlet	Emerald green
α-Naphthylamine	Crimson	Purple

3-*Nitro*-p-*phenylene*-1-*diazo*-4-*imine and its Acetyl Derivative.*

2-Nitro-*p*-phenylenediamine in dry acetone solution yielded on treatment with nitrous anhydride dissolved in the same solvent a diazo-derivative which separated as a brown, crystalline precipitate on adding dry ether at −15°. On attaining the ordinary temperature, this product resinified and lost its power of combining with β-naphthol to form an azo-derivative.

The acetyl derivative of this unstable diazo-compound was isolated by the following procedure. 4-Acetyl-2-nitro-*p*-phenylenediamine (1 gram) dissolved in 100 c.c. of dry acetone was treated successively with 10 c.c. of a 10 per cent. acetone solution of nitrous anhydride and 0·40 c.c. of acetic anhydride. The colour of the solution of the base changed from crimson to brown. The addition of 80 c.c. of ether produced a precipitate, probably consisting of unacetylated diazoimine, which dissolved again as acetylation proceeded, the acetyl derivative separating on the addition of a further 100 c.c. of ether in brownish-red plates exploding violently at 140°:

0·1500 gave 35·3 c.c. N_2 at 18° and 773·6 mm.* N = 27·70.
$C_8H_6O_3N_4$ requires N = 27·18 per cent.

*Constitution of 4-Acetyl-3-nitro-*p*-phenylene-1-diazo-4-imide.*

The azo-β-naphthol compound of 4-acetyl-3-nitro-*p*-phenylene-1-diazo-4-imide was a dark red powder melting above 290°. Its saturated solution in glacial acetic acid was diluted with three volumes of water and the liquid rendered alkaline with concentrated aqueous ammonia. This treatment led to hydrolysis of the acetyl group in the azo-derivative. The resulting 3-nitro-4-aminobenzeneazo-β-naphthol, a pale brown powder melting at 208°, and developing a claret coloration with concentrated sulphuric acid, was diazotised by adding nitrous acid at −10° to −15° to its solution in absolute alcohol. The diazo-compound gave with alkaline β-naphthol a brown bisazo-derivative, developing a yellow coloration with concentrated sulphuric acid.

On warming an alcoholic solution of the diazo-compound of 3-nitro-4-aminobenzeneazo-β-naphthol, nitrogen was evolved, and the liquid on evaporation left a dark, tarry mass from which 3-nitrobenzeneazo-β-naphthol was extracted on boiling with 80 per cent. alcohol and animal charcoal. The filtrate on cooling deposited bright yellowish-orange crystals which melted at 192°, and developed a bright cherry-red coloration with concentrated sulphuric acid. For the purpose of comparison, *m*-nitroaniline was converted successively into 3-nitrobenzenediazonium chloride and 3-nitrobenzeneazo-β-naphthol. The latter compound melted at 194° and gave a similar cherry-red coloration with concentrated sulphuric acid. The melting point of a mixture of the two preparations varied between 189° and 192°.

4-*Acetyl*-3-*nitro*-p-*phenylene*-1-*diazo*-4-*imide* gave the following

* In this and the following estimations the nitrogen was measured over 50 per cent. potassium hydroxide

colour reactions when converted into its azo-derivatives by combining in the presence of pyridine:

Azo-compound with:	Colour of azo-compound.	Coloration with concentrated sulphuric acid.
β-Naphthol	Brownish-red	Magenta red
β-Naphthylamine	Brownish-red	Brown
α-Naphthol	Reddish-brown	Olive green
α-Naphthylamine	Dark red	Magenta red

*Acetyl-*p*-diazoimides derived from* 2:6-*Dichloro-*p*-phenylenediamine.*

A solution of 1 part of *p*-nitroaniline in 3 parts of glacial acetic acid and 6 parts of concentrated hydrochloric acid was cooled to 0° and treated with chlorine until 2 molecular proportions of the gas had been used. The mixture was kept thoroughly stirred throughout the chlorination, and the lemon-yellow precipitate of 2:6-dichloro-4-nitroaniline was obtained in theoretical yield (compare Flürscheim, T., 1908, **93**, 1773). This nitro-compound (1 part) and ammonium chloride ($\frac{3}{8}$ part) were dissolved in 25 parts of 50 per cent. alcohol, and 1 part of zinc dust (80 per cent. Zn) was added slowly to the boiling solution. The mixture was heated under reflux for half an hour until the colour changed from yellow to light grey. The filtrate from the precipitate of zinc and zinc hydroxide was then distilled and the greater part of the alcohol thus recovered. 2:6-Dichloro-4-phenylenediamine separated from the residual solution in colourless plates, becoming brown with a bronzy reflex on exposure to the air. The yield was 90 per cent. of the calculated quantity.

*4-Acetyl-2:6-dichloro-*p*-phenylene-1-diazo-4-imide.*

2:6-Dichloro-*p*-phenylenediamine (1 part) dissolved in 50 parts of warm water was acetylated by the addition of 1 part of acetic anhydride. The solution, which was vigorously stirred during this reaction, became speedily filled with colourless crystals of 4-acetyl-2:6-dichloro-*p*-phenylenediamine. The crude product was then recrystallised from hot water, from which it separated in colourless needles melting at 200°. One part of this acetyl compound dissolved in 100 parts of dry acetone and cooled to −15° was diazotised with 8·5 parts of a 10 per cent. solution of nitrous anhydride in the same solvent. On adding 100 parts of dry ether, the diazoimide separated as a pale yellowish-white, microcrystalline precipitate:

0·1500 gave 23·2 c.c. N_2 at 18·5° and 773 mm. N = 18·27.

$C_8H_5ON_3Cl_2$ requires N = 18·25 per cent.

4-*Acetyl*-2:6-*dichloro*-p-*phenylene*-1-*diazo*-4-*imide* was obtained in almost colourless plates decomposing explosively at 138°. This diazoimide coupled additively with the following developers either in the dry state or when mixed with pyridine:

Developer.	Colour of Azo-compound.	Coloration with concentrated sulphuric acid.
β-Naphthol	Orange-red	Bluish-red
β-Naphthylamine	Brownish-red	Brown
α-Naphthol	Brownish-red	Green
α-Naphthylamine	Red	Reddish-brown
Chromotropic acid	Cerise	Olive green

1-*Acetyl*-3:5-*dichloro*-p-*phenylene*-1-*diazo*-4-*imide*.

(1) *Preparation from* 1-*Acetyl*-2:6-*dichloro*-p-*phenylenediamine*.—2:6-Dichloro-4-phenylenediamine (10 grams) was heated for one hour in a reflux apparatus with 10 c.c. of acetyl chloride, when diacetyl-2:6-dichloro-*p*-phenylenediamine separated on cooling. The crude product when crystallised from hot water melted at 254°. 1-Acetyl-2:6-dichloro-*p*-phenylenediamine was prepared by half hydrolysing the diacetyl compound. The latter was boiled for fifteen minutes with 30 parts of *N*-sodium hydroxide solution, when, on cooling, the monoacetyl derivative separated in lustrous, colourless plates which, after recrystallisation from water, melted at 218°. Three parts of 1-acetyl-2:6-dichloro-*p*-phenylenediamine dissolved in 120 parts of dry acetone were diazotised with 1 part of nitrous anhydride dissolved in 10 parts of the same solvent. During diazotisation, the solution was thoroughly stirred, when the colour changed to bright yellow; the precipitation of yellow diazoimide then commenced, and was completed by the addition of 60 parts of dry ether:

0·2050 gave 32·5 c.c. N_2 at 18° and 762 mm. N = 18·37.

$C_8H_5ON_3Cl_2$ requires N = 18·25 per cent.

1-*Acetyl*-3:5-*dichloro*-p-*phenylene*-1-*diazo*-4-*imide* is an orange-yellow, crystalline powder, very sensitive to light, changing rapidly to chocolate, and decomposing at 133°. It combined additively with the following developers on mixing either in the dry state or in pyridine:

Developer.	Colour of azo-compound.	Coloration with concentrated sulphuric acid.
β-Naphthol	Orange-red	Scarlet
β-Naphthylamine	Orange	Blue
α-Naphthol	Brownish-red	Green
α-Naphthylamine	Orange	Scarlet

(2) *Preparation from* 2:6-*Dichloro*-p-*phenylenediamine*.—2:6-Dichloro-*p*-phenylenediamine (1 part) dissolved in 40 parts of dry

acetone at −10° was diazotised with 0·85 part of nitrous anhydride in a 10 per cent. acetone solution. The solution, which was stirred mechanically, became slightly paler in colour, and on the addition of 2 parts of acetic anhydride gave a dark grey, flocculent precipitate. This substance, which decomposed explosively at 138°, was very sensitive to light and darkened on exposure:

0·2000 gave 33·25 c.c. N_2 at 19° and 759 mm. N = 19·11.

$C_8H_5ON_3Cl$ requires N = 18·25 per cent.

This specimen of diazoimide, combined in pyridine with the following developers, gave the same colour reactions as those obtained in the foregoing preparation:

Developer.	Colour of azo-derivative.	Coloration with concentrated sulphuric acid.
β-Naphthol	Orange-red	Scarlet
β-Naphthylamine	Orange	Blue
α-Naphthol	Brownish-red	Green
α-Naphthylamine	Orange	Scarlet

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XLVIII.—*A New Form of Methylgalactoside and its Conversion into Octamethyldigalactose and into a Methyldigalactoside.*

By MARY CUNNINGHAM.

THE isolation of a new form of methylglucoside by Fischer (*Ber.*, 1914, **47**, 1980), and the detailed study of its derivatives by Irvine, Fyfe, and Hogg (T., 1915, **107**, 524), naturally suggests the possibility that members of the dulcitol series of hexoses may also exhibit the same structural isomerism. Observations have, in fact, already been recorded indicating that galactose can react in a form other than the α- and β-modifications, and recently all doubt on this point has been removed by the preparation of four galactose pentaacetates by Hudson and his co-workers (*J. Amer. Chem. Soc.*, 1916, **38**, 1223). The first mention of this unexpected isomerism occurs, however, in Fischer's original description of the methylhexosides (*Ber.*, 1895, **28**, 1174). By concentrating an acid methyl-alcoholic solution of the crystalline α- and β-methylgalactosides, an amorphous product was obtained which Fischer regarded as a third form of methylgalactoside. The absence of analytical data

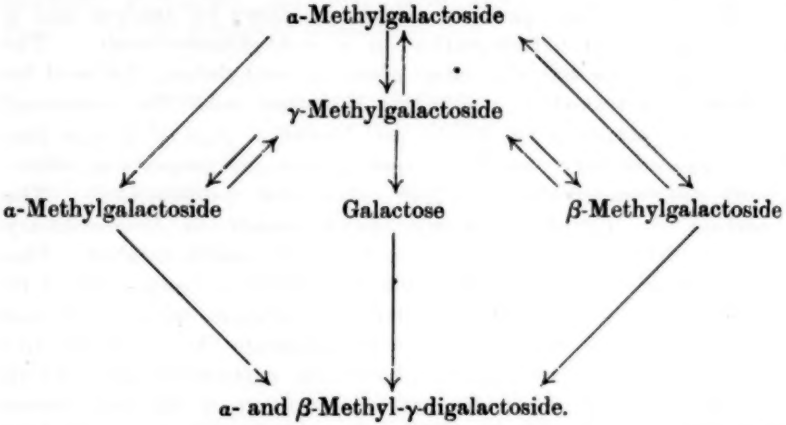
rendered complete identification of this substance impossible, and some years later Irvine and Cameron (T., 1905, **86**, 907) suggested that a methylated galactoside prepared by them and found to possess abnormal properties might be a derivative of the third isomeride referred to by Fischer. In this research, Irvine and Cameron isolated a syrupy form of methylgalactoside, which from its low specific rotation was at first regarded as consisting mainly of the β-modification. This particular methylhexoside is now shown to be a true methylgalactoside of the γ-series resembling γ-methylglucoside in its properties, but it is not identical with Fischer's amorphous product, which, as shown by analysis and a molecular weight determination, is a *methyldigalactoside*. The new form of methylgalactoside gives on methylation, followed by hydrolysis, tetramethyl γ-galactose, identical with the compound previously prepared by Irvine and Cameron (*loc. cit.*), and this sugar has now been found to possess the unique property of undergoing auto-condensation to give octamethyl γ-digalactose. The reaction in question proceeds spontaneously at the ordinary temperature and in the absence of any recognisable catalyst. This is, of course, a most unusual result, and, taken in conjunction with the formation, in somewhat similar circumstances, of a substituted disaccharide derivative from γ-methylglucoside (Irvine, Fyfe, and Hogg, *loc. cit.*), it serves to emphasise the extraordinarily reactive character of ethylene–oxide sugars. Moreover, it has been shown that the reaction which gives rise to methyldigalactoside also involves the presence—probably only transitory—of a variety of galactose conforming to this particular type of sugar. This conclusion seems warranted by the fact that the digalactoside, as shown by a study of its behaviour on hydrolysis, consists of the stable forms of methylgalactoside (α- and β-) united to the unstable form of the sugar. The union involves the reducing group of the latter, and accordingly the structure of the complex is represented by the formula

$$\mathrm{MeO{\cdot}CH{\cdot}[CH{\cdot}OH]_2{\cdot}CH{\cdot}CH(OH){\cdot}CH_2{\cdot}O{\cdot}CH{\cdot}CH{\cdot}[CH{\cdot}OH]_3{\cdot}CH_2{\cdot}OH}$$

(the CH·O·CH bridge forming a three-membered ring)

A significant observation is that no structural modification of the digalactoside can be obtained by varying the form of methylgalactoside employed in its preparation. Thus, whether the starting point is an acid, methyl-alcoholic solution of pure α-, pure γ-, or an equilibrium mixture of α- and β-methyl-galactosides, a compound having the same constants and properties and giving the same results on hydrolysis is formed in each case. The most prob-

able explanation of this rather surprising result seems to be that under the influence of acid methyl alcohol, any one form of methylgalactoside passes to an equilibrium mixture of the three isomerides α-, β-, γ-, and of these the unstable γ-variety is subsequently hydrolysed on concentration to give the reactive type of the sugar. This immediately combines with the stable hexosides to give a non-reducing complex, regeneration of γ-methylgalactoside being impossible owing to the removal of the alcohol. The course of the reaction would be represented by the following scheme:



These suggestions are, moreover, in accord with the results previously obtained by Irvine and Cameron (T., 1905, **86**, 907), who found that fully methylated hexosides of stable form could be heated at 110° to 150° without any hydrolysis occurring, the only change observed being an interconversion to an equilibrium mixture of the α- and β-isomerides. In these experiments, the formation of the γ-variety was impossible owing to the presence of the methoxyl groups, so that the complicated reactions described above could not take place.

Experimental.

γ-Methylgalactoside.—Galactose was heated at 100° with methyl alcohol containing 0·25 per cent. of hydrogen chloride in essentially the way described by Fischer for the preparation of α- and β-methylgalactosides, except that the acid was neutralised before removing the solvent. The neutralised solution deposited crystals of α-methylgalactoside on slight concentration, and from the filtrate a viscid syrup was obtained on further heating. On the addition of ether, this syrup formed a semi-solid mass consisting for the

most part of α- and β-methylgalactosides, but on triturating the mass with small quantities of absolute alcohol, some of the adhering syrup passed into solution and was removed by filtration. In this manner, a nearly colourless syrup of a non-reducing character was prepared which, in order to remove impurities, was dissolved in methyl alcohol and the solution fractionally precipitated by successive additions of ethyl acetate. The yield was 30 per cent. of the sugar used. For analysis, the syrup was dried to constant weight at 60°/20 mm. This method of preparation, it will be observed, differs considerably from that described by Fischer (*loc. cit.*) for the isolation of γ-methylglucoside, and it seems to point to the interesting conclusion that in the ordinary process of hexoside synthesis, the three modifications, α-, β-, and γ-, are produced together.

Found: C = 42·94; H = 7·3; OMe = 15·7.

$C_7H_{14}O_6$ requires C = 43·27; H = 7·27; OMe = 15·98 per cent.

The new compound thus isolated as a mixture of stereoisomerides showed the characteristic reactions of derivatives of the γ-series and gave $[\alpha]_D$ +12·95° in methyl alcohol and +25·9° in water. It should be mentioned that attempts to prepare acetone derivatives similar to γ-methylglucosidemonoacetone were entirely unsuccessful.

Hydrolysis of γ-Methylgalactoside.—γ-Methylgalactoside is somewhat more stable towards dilute acids than the corresponding glucoside, as it is necessary to carry out the hydrolysis with *N*/100-hydrochloric acid at 100°. The changes in optical activity observed are shown in Fig. 1, and it will be seen that the specific rotation increases without any irregularities until the value for galactose is reached, at the end of four and a-half hours. The continuity of the curve might at first suggest that only one of the two possible modifications of the ethylene–oxide type was present, but subsequent methylation showed the existence of the two varieties. The form of the curve does, however, prove that Fischer's amorphous product cannot be one of these γ-isomerides. This compound is more dextrorotatory than galactose itself, and if it were present, the curve would show a point above the specific rotation of galactose before the constant value was reached.

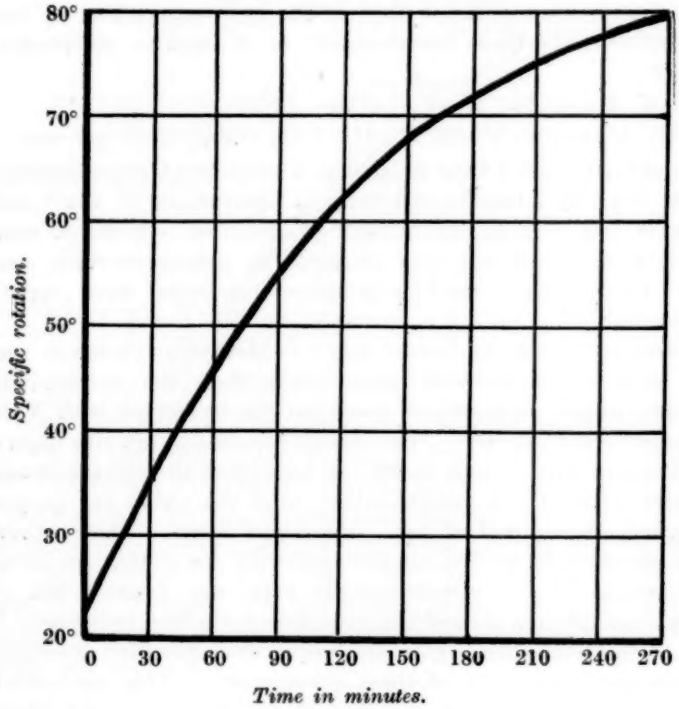
Tetramethyl γ-Methylgalactoside.—γ-Methylgalactoside was methylated by the silver oxide method under the usual conditions, and the alkylation proceeded normally. After three methylations, the product was extracted with ether, and on distilling at 142—145°/12 mm., a colourless, mobile liquid was obtained having $[\alpha]_D$ +3·98° in alcohol. The value given by Irvine and Cameron for their abnormal form of tetramethyl methylgalactoside was

+4·06°, so that the two compounds are identical. Fractionation separated the distillate into two portions; the one boiling at 135°/12 mm. gave $[\alpha]_D$ −4·3°, and the other, boiling at 150°/12 mm., showed $[\alpha]_D$ +8·8°, but the analytical composition of each fraction was identical.

Hydrolysis of Tetramethyl γ-Methylgalactoside, Tetramethyl γ-Galactose, and Octamethyl γ-Digalactose.—The methylated galactoside is only completely converted into the corresponding

FIG. 1.

Hydrolysis of γ-methylgalactoside.

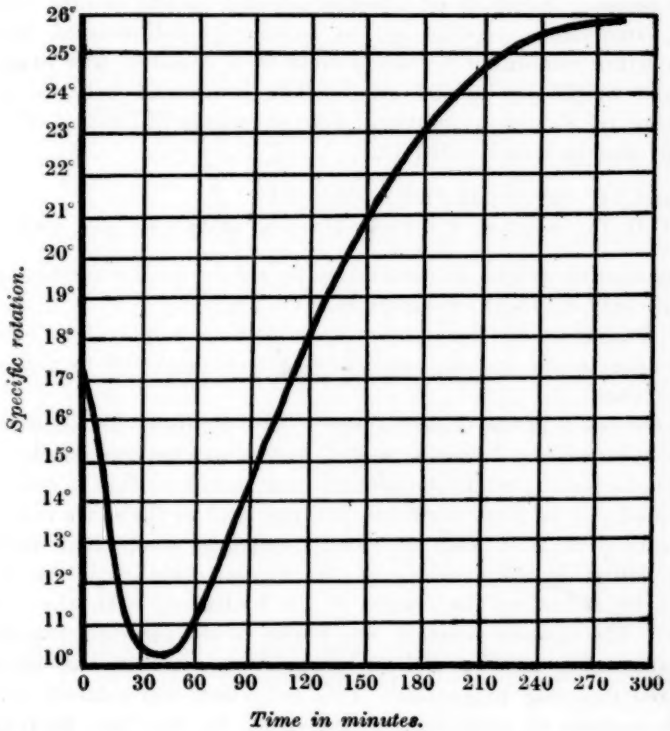


sugar by heating at 100° with *N*/100-hydrochloric acid for eight hours, and consequently hydrolysis experiments were carried out with *N*/10-acid at 100°. As shown on the accompanying curve (Fig. 2), the specific rotation falls initially and then rises, the constant value +25·9° being reached at the end of five hours. The specific rotation given by Irvine and Cameron (*loc. cit.*) for the methylated sugar was 26·1°, so that there was no doubt that tetramethyl γ-galactose was present, but as new and unexpected cases

of auto-condensation had recently been observed, the sugar, isolated as usual, was left to remain for some time before distillation with the idea that a disaccharide derivative might possibly be formed. After an interval of seven days, the syrup was distilled at the low pressure of the Gaede pump. The distillate (b. p. 114—117°/ 0·03 mm.), which was a colourless syrup, had now lost the properties of a reducing sugar and acquired those of a glucoside. More-

FIG. 2.

Hydrolysis of tetramethyl γ-methylgalactoside.



over, the specific rotation had increased greatly, the values for $[\alpha]_D$ in alcohol and water being $+54{\cdot}4°$ and $+75°$ respectively. As was to be expected, the new compound reduced potassium permanganate solution instantaneously.

Found: C = 52·2, 52·4; H = 8·5, 8·7; OMe = 57·1, 57·3.

$C_{20}H_{38}O_{11}$ requires C = 52·86; H = 8·4; OMe = 54·6 per cent.

The analytical figures indicate that the compound is octamethyldigalactose; but it is obviously not quite pure.

Hydrolysis of Octamethyl γ-Digalactose.—On heating a solution of the methylated disaccharide in $N/10$-hydrochloric acid at 100°, the specific rotation decreased, and at the end of eight and a-half hours reached the constant value $+25{\cdot}6°$, which agrees with the figure previously found for tetramethyl γ-galactose, and establishes the compound as essentially a disaccharide derivative.

Methyldigalactoside (1) *from α- and β-Methylgalactosides.*—A solution of 10 grams of an equilibrium mixture of α- and β-methylgalactosides in 50 c.c. of methyl alcohol was concentrated to a viscid syrup, which was dissolved in methyl alcohol and the solution filtered. Addition of absolute alcohol to the filtrate gave a white, amorphous product of an extremely deliquescent nature which, after remaining for some time in a vacuum, was dried to constant weight at 70°/20 mm. The compound behaved as a glucoside to Fehling's solution, and gave $[\alpha]_D$ in methyl alcohol $+85{\cdot}6°$ and in water $+101{\cdot}1°$.

Found: C = 43·88; H = 6·9; OMe = 9·05.

$C_{13}H_{24}O_{11}$ requires C = 43·8; H = 6·8; OMe = 8·7 per cent.

A molecular weight determination by the cryoscopic method gave M.W. = 341; $C_{13}H_{24}O_{11}$ requires M.W. = 356.

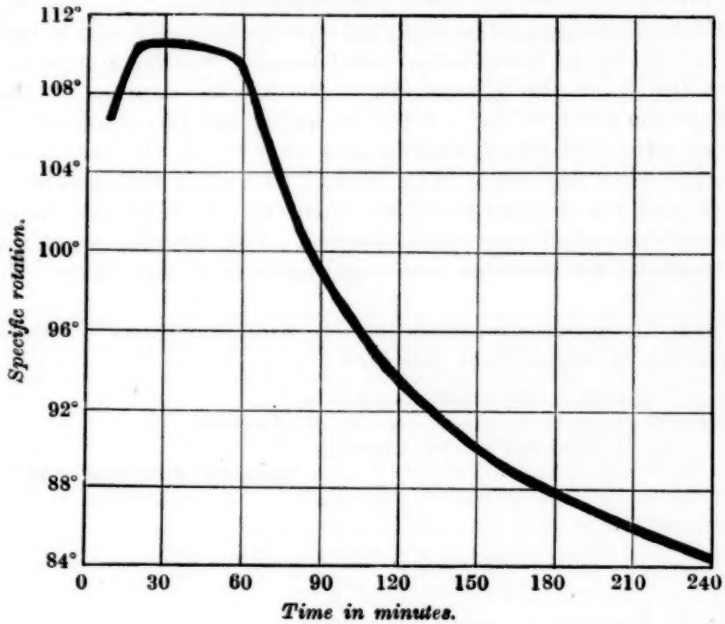
An estimation by the ebullioscopic method could not be carried out, owing to the sparing solubility of the compound in any suitable solvent.

Hydrolysis of Methyldigalactoside.—The digalactoside showed the marked instability towards neutral potassium permanganate solution characteristic of ethylene–oxide compounds, so that it evidently contained one or more unstable linkings, and as these are ruptured by heating at 100° with $N/100$-hydrochloric acid, their number and position in the molecule of the digalactoside could be ascertained by following the course of the hydrolysis with the polarimeter. The specific rotation was found to increase and reached a constant value at the end of three hours, whilst the solution acquired reducing properties. This reduction was entirely due to the formation of galactose, as indicated by the fact that treatment with phenylhydrazine yielded galactosephenylosazone alone. At the same time, a methoxyl estimation carried out on the products isolated at this first stage of the hydrolysis showed that a hexoside was present. Hence the increase in specific rotation is not due to the formation of a disaccharide, but is occasioned by the liberation of α-methylgalactoside, $[\alpha]_D + 180°$. The molecule of the digalactoside therefore contains only one unstable linking, which is situated in one of the sugar residues, and the stability of the glucosidic methyl group shows that this portion of the molecule

retains the normal butylene–oxide structure. These observations are summarised in the constitutional formula given on p. 597 The maximum value for the optical activity is, however, less than that required for an equimolecular mixture of α-methylgalactoside, $[\alpha]_D$ +180°, and galactoside, $[\alpha]_D$ +81°. This deficiency is most likely due to the presence of the practically inactive β-methylgalactoside, and the form of the rotation curve when the hydrolysis is carried out with *N*/10-hydrochloric acid supports this contention. The changes in specific rotation are shown in Fig. 3, and it will be

FIG. 3.

Hydrolysis of methyldigalactoside.



observed that the rapid rise to the maximum value in the first twenty minutes is succeeded by a constant period of forty minutes, during which the decline in activity due to the hydrolysis of the α-isomeride is balanced by the increase in activity occasioned by the more quickly hydrolysed β-form, whilst the marked fall in the next ten minutes indicates that this masking effect has now disappeared. The specific rotation then decreases regularly until the value for galactose is reached after four hours. This preparation of the digalactoside therefore undoubtedly consists of α- and β-methylgalactosides in union with γ-galactose.

Methyldigalactoside (2) *from γ-Methylgalactoside.*—γ-Methylgalactoside was treated in the same way as the mixture of α- and β-methylgalactosides. The compound isolated gave the same values for the specific rotation as the previous preparation, +85·6° in methyl alcohol and 101·1° in water. On hydrolysis with *N*/100-hydrochloric acid at 100°, the specific rotation increased to the constant value +109·6° at the end of three hours, and after the acid concentration had been raised to *N*/10, the same characteristic points were observed as before. The specific rotation remained constant for forty minutes, and then fell sharply to 104·5° in the next twenty minutes, after which it decreased steadily until the hydrolysis was complete.

Methyldigalactoside (3) *from α-Methylgalactoside.*—In this experiment, a specimen of α-methylgalactoside was used which had been several times recrystallised until entirely free from traces of either the β- or the γ-isomeride. The specific rotation of the digalactoside obtained was +100·9° in water, and this increased on heating with *N*/100-hydrochloric acid at 100° to the maximum value 110·3° at the end of three hours. Thereafter the concentration of acid was changed as before, when the variations in activity previously described were again observed. The preparations of the digalactosides are therefore indistinguishable from each other.

I wish to express my indebtedness to Professor Irvine for valuable advice in carrying out this work.

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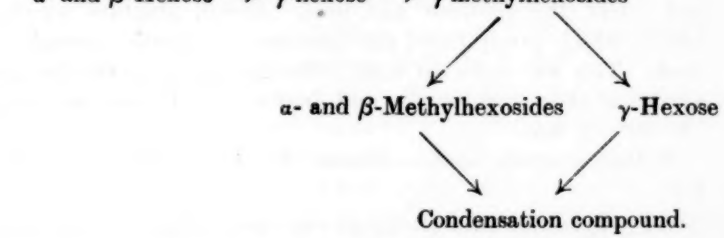
[*Received, April 23rd,* 1918.]

XLIX.—*The Application of the Auto-condensation Powers of γ-Sugars to the Synthesis of Carbohydrate Complexes.*

By MARY CUNNINGHAM.

THE preparation of γ-methylglucosidemonoacetone (Macdonald, T., 1913, **103**, 1896; Irvine, Fyfe, and Hogg, T., 1915, **107**, 524) and a comparison of the conditions under which the stable and unstable hexosides are formed suggest that the initial action of acid methyl alcohol on a reducing sugar may consist in transform-

ing a portion of it from the normal to the reactive form. This form of the sugar seems incapable of existence in the free state, and hence it would immediately combine with the alcohol to form a γ-methylhexoside. In the preceding communication it has been shown that if a solution of any one of the three isomeric methyl-galactosides in acid methyl alcohol is concentrated, then a mixture of stereoisomeric condensation compounds results consisting of the stable hexosides united to γ-galactose. It seemed, therefore, not impossible that similar compounds might be formed by merely dissolving a reducing sugar in this reagent and concentrating the solution. The course of the anticipated reaction is represented by the following scheme:



It was, of course, recognised that as the reaction could not be readily controlled, the γ-sugar formed might condense either with the stable hexosides or with a preformed complex, thus giving rise to products of greater complexity than the methyldigalactoside referred to, or even to mixtures of different complexes. These ideas were realised in that compounds containing two or more sugar molecules were obtained, galactose and dextrose giving respectively a methyltetragalactoside and a methyltetraglucoside, $C_{25}H_{44}O_{21}$, whilst maltose yielded a methyltrimaltoside,

$$C_{37}H_{64}O_{31},H_2O.$$

Compounds of a similar nature could not be prepared from fructose, as charring invariably occurred on concentrating a solution of the sugar in acid methyl alcohol, and, among the reducing disaccharides, lactose remained entirely unaffected by the reagent. The products behaved as glucosides towards Fehling's solution and showed the characteristic reactions of γ-compounds, whilst the results obtained on hydrolysis indicate that they are constituted similarly to methyldigalactoside, the glucosidic methyl group being attached to a sugar residue retaining the normal butylene–oxide structure, whilst the remaining sugar residues conform to the ethylene–oxide type. It should be mentioned that estimations of methoxyl have been chiefly relied on in establishing the degree of

complexity of these derivatives. Elementary analysis is obviously of little assistance, and the presence of so many hydroxyl groups rendered accurate determinations of molecular weight impossible, especially as water was the only solvent that could be employed.

Experimental.

The same method of preparation was adopted in each case. Ten grams of finely powdered sugar were added gradually to 50 c.c. of methyl alcohol containing 0·25 per cent. of hydrogen chloride, and the mixture was gently warmed, if necessary, to hasten solution. The solution was then concentrated on a steam-bath to a viscid syrup, which was dissolved in a small quantity of methyl alcohol, and, after the solution had been filtered, absolute alcohol was added, which precipitated the complex as a white, amorphous product. This was collected with difficulty, owing to the deliquescent nature of these compounds, and finally dried to constant weight at 70—80°/12 mm.

Methyltetragalactoside.—Found: C = 44·16; H = 6·8; OMe = 4·3, 4·0.

$C_{25}H_{44}O_{21}$ requires C = 44·12; H = 6·5; OMe = 4·5 per cent.

$[\alpha]_D$ in water = 94·0° (c = 1·6590).

Hydrolysis of Methyltetragalactoside.—On heating at 100° with N/100-hydrochloric acid, the specific rotation increased to the constant value +108·5° at the end of five hours. Galactosephenylosazone alone was isolated at this stage, so that the increase in optical activity is probably due to the presence of α-methylgalactoside. Thereafter, the acid concentration was raised to N/10, and some of the polarimetric changes observed are shown below:

Initial specific rotation.....	+108·5°
After 320 minutes at 100°	108·5
„ 340 „ „	106·0
„ 360 „ „	100·0
„ 420 „ „	94·0
„ 540 „ „	86·8 (constant)

As in the case of methyldigalactoside, the presence of β-methylgalactoside seems established by the fluctuations in activity recorded in the first sixty minutes. The final optical value when corrected for the calculated weight of sugar formed on the basis of the suggested formula for the compound becomes +82·0° (galactose = +81·0°).

Methyltetraglucoside.—Found: C = 43·5; H = 6·6; OMe = 4·96.

$C_{25}H_{44}O_{21}$ requires C = 44·12; H = 6·5; OMe = 4·5 per cent.

$[\alpha]_D$ in water = 98·1° (c = 0·9070).

Hydrolysis of Methyltetraglucoside.—The specific rotation increased on partial hydrolysis with $N/100$-acid at 100° to the value +104·5° at the end of sixty minutes, and then declined steadily, the final value, +87·5°, being reached at the end of four hours. The initial rise and subsequent fall probably indicate, as in the case of the galactose derivative, that both α-methylglucoside, $[\alpha]_D$ +157°, and β-methylglucoside, $[\alpha]_D$ −33°, are present. On completing the hydrolysis with $N/10$-acid, the optical activity continually declined, reaching the constant value +57·3° after heating for a further six hours. Calculating on the above formula, this gives +54·1° as the actual value for the specific rotation, which again is not far removed from the theoretical number +52·5°.

Methyltrimaltoside.—This compound, even after drying to constant weight at 70°/40 mm., retained a molecule of water, which was only removed on further heating at 100°/40 mm.

Found: C = 43·0, 43·0; H = 6·6, 6·7; OMe = 3·6, 3·5; H_2O = 1·5.
$C_{37}H_{64}O_{21},H_2O$ requires C = 43·4; H = 6·5; OMe = 3·0; H_2O = 1·7 per cent.

$[\alpha]_D$ in water +124·0° (c = 1·057).

Hydrolysis of Methyltrimaltoside.—After heating with $N/100$-hydrochloric acid at 100° for three hours, the specific rotation had declined to the constant value +113·6°, when maltosephenylosazone was isolated, but on further hydrolysis with $N/10$-acid the activity continued to decline, showing that both the maltoside and the maltose were undergoing hydrolysis. The final value, +56·8° (corrected, +53·7°), was obtained at the end of ten hours.

The author desires to express her thanks to Professor Irvine for the advice and assistance which she has received.

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L.—*The Preparation of a New Type of Organic Sulphur Compound.*

By Gerald Noel White.

The compound which forms the subject of this paper is a representative of a class of compounds which, so far as can be ascertained, has hitherto eluded isolation, being a derivative of hydrogen persulphide, H_2S_2, in the form of *β-naphthylthiosulphoxylic acid*:

It is highly probable that compounds of this type are produced as intermediate products in a number of chemical processes. In particular, the production of the sulphide dyes in all probability involves the formation of analogous derivatives of hydrogen disulphide.

The compound in question is produced by gently heating together molecular quantities of β-naphthyl disulphide, sodium sulphide crystals, and pure sulphur. After complete solution of the sulphur in the aqueous sodium sulphide, the naphthyl disulphide passes slowly into solution with continued heating to about 80°.

On cooling, glistening lamellæ of the *sodium* salt, which is very readily soluble in water, crystallise out. Purification is difficult, but after pressing on a porous plate, the most satisfactory method is to dissolve the sodium salt in alcohol and precipitate it with benzene.

For analysis, a portion of the sodium salt prepared in this way was treated with aqueous hydrochloric acid. The free acid was dissolved in alcohol and precipitated with water; this process was repeated three times and the product dried in a desiccator:

0·1757 gave 0·4044 CO_2 and 0·0569 H_2O. C = 62·8; H = 3·6.
0·1136 gave 0·2827 $BaSO_4$. S = 34·1.

$C_{10}H_8S_2$ requires C = 63·1; H = 3·2; S = 33·7 per cent.

With lead acetate, a deep orange precipitate is obtained, which darkens to scarlet on keeping, and ultimately changes to deep brown or black by decomposition to lead sulphide.

If this reaction is allowed to proceed in boiling alcohol, and the clear solution decanted quickly, crystals of β-naphthyl disulphide are formed on cooling which are remarkable for their purity. A study of this reaction failed to detect any deposition of sulphur as should result from the decomposition of a normal

lead salt, and it seems probable that the alcohol used in the reaction may act as a reducing agent, which would explain this observation.

At present, however, the evidence is insufficient to do more than indicate the possible course of the reaction.

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LI.—*Double Carbonates of Sodium and Potassium with the Heavy Metals.*

By MALCOLM PERCIVAL APPLEBEY and KENNETH WESTMACOTT LANE.

THE combination of alkali carbonates with carbonates of the heavy metals to form crystalline double salts has been long known, many of these compounds having been prepared by Deville (*Ann. Chim. Phys.*, 1851, [iii], **33**, 75) by digesting the precipitated metallic carbonate with excess of a concentrated solution of the alkali carbonate. Double carbonates of cobalt, nickel, zinc, and magnesium with potassium, and of copper, magnesium, cobalt, nickel, and zinc with sodium, were thus prepared, whilst several double bicarbonates were obtained in a similar manner. Owing to the method of preparation adopted, Deville's compounds must have been contaminated with normal and basic metallic carbonates, but his products were sufficiently pure to make possible a general characterisation of this group of substances. A somewhat more satisfactory method of preparation was adopted by Reynolds (T., 1898, **73**, 262), who ground the solid acetate of the metal with a concentrated solution of potassium carbonate. Under these conditions, complete solution takes place, and the crystalline double carbonate is subsequently deposited in a fairly pure state. In this way, Reynolds succeeded in obtaining the double carbonate of copper and potassium which Deville had failed to prepare owing to its great solubility. The analyses of Reynolds's copper compounds show rather high values for the copper content, and suggest the presence of basic carbonate. Gröger (*Ber.*, 1901, **34**, 429) afterwards demonstrated the advisability of adding bicarbonate to the alkaline carbonate solution, a modification which, as was pointed out by Wood and Jones (*Proc. Camb. Phil. Soc.*, 1907, **14**, 71), represses the hydrolytic dissociation of the copper carbonate. The potassium and sodium copper carbonates prepared by Gröger never-

theless contained considerable amounts of basic carbonate, the potassium salt being particularly impure. This was, however, probably due to the subsequent treatment of the salts.

The nature of the deep blue solutions from which the copper salts are deposited has been examined by Luther and Krˇnjavi (*Zeitsch. anorg. Chem.*, 1905, **46**, 170), who proved by transport experiments the presence of a deep blue complex negative ion containing copper. The conditions under which crystallisation of double salts from such solutions takes place have also been discussed by Deville and by Gröger. No quantitative study of these conditions has yet, however, been attempted, although the case is one of particular interest, since it relates to a double salt of which one constituent is practically insoluble in water. The authors therefore undertook a study of the solubility equilibria in the case Na_2CO_3–$Na_2Cu(CO_3)_2$–$CuCO_3$, which is typical of double salt equilibria of this kind. It was hoped that a parallel investigation of the equilibria in the formation of the potassium cobalt compound would be of interest. Unfortunately, owing to the difficulties of analysis in the latter case and to the enforced suspension of the work under present conditions, it has not been found possible to bring this part of the investigation to a satisfactory conclusion. The present communication therefore deals almost entirely with the sodium copper carbonate equilibrium.

Preparation and Properties of the Double Salts.

The salts prepared for the purpose of this investigation were all obtained by a method which, whilst not giving so good a yield as could be obtained by Reynolds's method, was preferable for the purpose in view, since it gave products of greater purity, analysis showing that the amount of basic carbonate present was small.

Sodium Copper Carbonate.—A solution was prepared containing about 100 grams of sodium carbonate (anhydrous) and 40 grams of sodium bicarbonate in a litre. To this solution, at a temperature of about 50°, a concentrated solution of cupric acetate was added from a burette with a fine point, the liquid being stirred continually during the addition. A clear, deep blue solution quite free from suspended basic carbonate is obtained in this way. The amount of cupric acetate solution to be added is found by trial; if too much is added, precipitation of basic carbonate occurs; if too little, there is no crystallisation. The solution is filtered and left to remain overnight, when a deposition of well-formed crystals of the double salt takes place. These are collected, rapidly washed with

pure alcohol, and dried in a desiccator. The mother liquor can be used for a further preparation, and gives a rather better yield.

The salt, which crystallises in needles or rosette-like agglomerations, dries to a constant weight in a desiccator. It is, in fact, a more stable substance than might be expected, since microscopic examination fails to show any alteration in the transparency of the crystals after they have been kept at the temperature of boiling water for a considerable time. At higher temperatures, the substance loses water and carbon dioxide, passing through a stage when it has a purple colour, and giving finally a mixture of cupric oxide and sodium carbonate. It is decomposed by water, but dissolves in and can be recrystallised from a concentrated solution of sodium carbonate containing bicarbonate. This observation, which is in direct contradiction to the experience of Gröger (*loc. cit.*), has been fully established by repeated tests.

The copper in the compound was determined by the sulphide method and also electrolytically, the sodium as sulphate after precipitation of the copper. Carbon dioxide and water were estimated directly in the usual manner.

Found: Cu = 22·05; Na = 16·05; CO_3 = 42·52; H_2O = 19·62.

$Na_2Cu(CO_3)_2,3H_2O$ requires Cu = 22·40; Na = 16·21; CO_3 = 42·37; H_2O = 19·02 per cent.

It will be seen that the substance has the formula

$$Na_2Cu(CO_3)_2,3H_2O,$$

as was found by Deville, Gröger, and Wood and Jones (*loc. cit.*). The amount of water of crystallisation in this salt is somewhat anomalous, as the large number of double carbonates of potassium investigated by Reynolds, and the sodium cobalt compound to be described later, all crystallise with four molecules of water.*

Sodium Cobalt Carbonate.—This substance was prepared in exactly the same manner as the copper compound, except that the cobalt was added in the form of nitrate solution. The double salt crystallises in crusts of fine crystals of a very bright reddish-purple colour. It can be recrystallised from a solution of sodium carbonate and bicarbonate, but it is difficult to obtain well-formed crystals.

The salt was analysed by dissolving a weighed quantity in excess of standard acid and titrating with standard alkali, using methyl-orange as indicator. The colour of the solution is not sufficiently intense to affect the accuracy of this determination, which gives the total basic equivalent of the sodium and cobalt in the compound. Another weighed sample is then ignited until it is completely con-

* The potassium copper salt can also be obtained anhydrous and with one molecule of water, but not with three.

verted into a mixture of cobalt oxide and sodium carbonate, of which the latter can be extracted with hot water and estimated by titration. This gives the percentage of sodium in the compound and the percentage of cobalt by comparison with the determination of total basic value. The sodium was also determined as sulphate (*a*). The water was determined in the usual way and the carbon dioxide by difference.

Found: Co = 20·42; Na = 15·03, 15·26(*a*); CO_3 = 40·79; H_2O = 23·64.

$Na_2Co(CO_3)_2,4H_2O$ requires Co = 19·85; Na = 15·52; CO_3 = 40·38; H_2O = 24·25 per cent.

The substance evidently has a formula corresponding with the double potassium salts described by Reynolds, and is therefore unlike the sodium copper carbonate, which has only three molecules of water of crystallisation. Deville also obtained a double sodium cobalt carbonate with ten molecules of water, but this substance was not formed under the conditions described in this paper.

Potassium Cobalt Carbonate.—This salt is obtained in an analogous manner to those previously described, the solution used for the preparation containing about 400 grams of potassium carbonate and 100 grams of potassium bicarbonate per litre. On addition of cobalt nitrate solution, a dark, reddish-purple solution is obtained very similar in appearance to that from which the sodium salt is deposited. The crystalline double salt is, however, different in habit and in appearance from the corresponding sodium compound. The crystals are well formed and do not mass together in compact crusts. They present the appearance of six-sided tables which have not the bright purple tint of the sodium salt. Large crystals formed by evaporation of solutions saturated with the double salt have a red colour resembling ordinary cobalt compounds, whilst the smaller crystals deposited from the purple solutions are a lighter red, or in some cases a pale pink. The differences in colour between different specimens at first led to the belief that the cobalt potassium compound occurred in several forms differing either in composition or in crystalline form. Repeated analyses and measurements of solubility failed, however, to show any difference between the differently coloured specimens, nor did either the red form or the pink form grow at the expense of the other when both were kept in contact with a saturated solution for several months. The authors are therefore bound to conclude that the differences of colour referred to are not due to differences of composition, structure, or crystalline arrangement. They are probably to be explained by occlusion of different amounts of some colloidal substance, such as cobalt

carbonate. This conclusion is supported by the observation that increase in the concentration of bicarbonate in solution tended to favour the production of the lighter coloured variety. The effect is probably quite parallel with the well-known changes in the colour of many metallic salts when crystallised from solutions of varying acidity; these changes have been shown to be due to the occlusion of varying quantities of metallic hydroxides under different conditions.

Analysis by the method used for the sodium cobalt compound gave:

Found: Co = 17·85; K = 24·05; CO_3 = 21·60; H_2O = 36·50.

$K_2Co(CO_3)_2,4H_2O$ requires Co = 17·91; K = 23·72; CO_3 = 21·89; H_2O = 36·45 per cent.

This substance also clearly belongs to the normal type with four molecules of water of crystallisation, as was previously found by Reynolds.

Both the sodium and potassium cobalt salts have properties very similar to those of the sodium copper carbonate. They are quite stable in the cold, but lose water and carbon dioxide on heating. They are decomposed by water, but, like the copper compound, can be recrystallised from concentrated solutions of alkali carbonate and bicarbonate.

Formation of the Double Salts.

The formation of the double salts from the intensely coloured solutions has already excited some interest. Deville remarked upon the deep colour of the solutions, and doubted whether this colour could possibly be due to the small quantity of double carbonate which in the solid state is not more highly coloured than ordinary copper salts. A very striking experiment illustrating Deville's argument consists in acidifying a solution of the double carbonate containing 0·1 to 0·2 gram of copper per litre. This solution, which is bright blue, becomes almost colourless when the complex ion is destroyed by acidification, and even the addition of ammonia only produces a colour very much fainter than that of the original solution. Deville was so much impressed with the intense colour of the solutions that he regarded it as possible, if not probable, that the solutions contained some substance much more intensely coloured than the double carbonate into which it was slowly transformed during the crystallisation of the latter.

Other phenomena now to be discussed give considerable support to Deville's hypothesis. The crystals of the double salt are formed slowly from the solution when the latter has been kept for several hours, but the solution is not supersaturated in the ordinary sense.

This is shown by the fact that addition of crystalline nuclei does not appreciably hasten the separation. Gröger, who noted this phenomenon, also describes a remarkable experiment, which the authors have been unable to confirm. According to him, if a solution supersaturated with sodium bicarbonate is used in the preparation of the copper solution, addition of the crystalline double salt brings about no crystallisation, but sowing with a fragment of sodium bicarbonate not only induces crystallisation of the bicarbonate itself, but also brings about the rapid separation of the double salt along with it. This would constitute a remarkable type of supersaturation; attempts to repeat the experiment, however, never led to the result described, only bicarbonate being obtained as solid phase, whilst no appreciable fall in copper concentration took place.

It was thought that evaporation or absorption or loss of carbon dioxide might be a determining factor. Experiments were therefore entered on to test these points, but the results were entirely negative. Whether the solutions were left to crystallise in the open, in sealed flasks, or in a desiccator connected to a Kipp's apparatus for carbon dioxide, no appreciable difference in the rate of crystallisation was observed. It is therefore tentatively suggested that the behaviour of the solutions is due to one of the following causes:

(1) The rate of crystallisation is very small, and there are no stable supersaturated solutions.

(2) An intermediate compound is formed in the solutions which changes only slowly into the practically insoluble double salt.

In the latter case, the change from intermediate compound to double salt is reversible, since the double salt can be recrystallised from a solution of carbonate and bicarbonate.

The Solubility Equilibria.

In undertaking this investigation, the authors were faced at the outset with the difficulty that solutions of the double salts are unstable in absence of bicarbonate. Repeated attempts to obtain a solution saturated with sodium carbonate decahydrate and with the sodium copper carbonate in absence of bicarbonate all led to failure. When the solids were stirred in a constant-temperature bath at 18°, a blue solution was obtained, but decomposition with precipitation of basic compounds always occurred before the experiment had proceeded a sufficiently long time to ensure the attainment of equilibrium. It was therefore decided that the work must be carried out exclusively with solutions containing bicarbonate.

In many respects, the simplest plan and that promising results of most interest was to work with solutions saturated with sodium carbonate or with sodium bicarbonate, and the determinations made by the authors relate only to such solutions. The equilibria investigated are therefore those of (1) sodium copper carbonate and sodium bicarbonate with solutions containing increasing quantities of sodium carbonate; (2) sodium copper carbonate and sodium carbonate decahydrate with solutions containing decreasing quantities of bicarbonate. In each of these regions we are dealing with a system univariant at constant temperature with two solid phases. At the point of intersection we have at constant temperature a non-variant system with three solid phases.

The concentration of copper in the equilibrium solutions is in all cases very small in comparison with the concentrations of the sodium salts. The latter may consequently be considered as influenced only to an inappreciable extent by the presence of copper. The determinations therefore serve also to characterise the equilibrium of sodium carbonate and sodium bicarbonate at the temperature of experiment. They may be compared with the results of McCoy and Test (*J. Amer. Chem. Soc.*, 1911, **33**, 473) at 25°.

The solutions were prepared in a stirring-bottle closed with a mercury seal and maintained at 18° by means of a constant-temperature bath regulating to 0·02°. The time allowed for equilibrium to be established was never less than forty hours, preliminary experiments having shown that this was a satisfactory minimum period. When saturation was complete, the stirrer was stopped and the solution was allowed to settle. The stirrer was then removed and replaced by an inverted filter, through which the saturated solution was blown into a clean flask, from which samples were taken for analysis. Filtration of the solutions was necessary, as in some cases a solid substance, probably a basic carbonate, was present in a state of very fine suspension.

The concentration of copper in the solutions was found by direct titration of the solutions with a potassium cyanide solution, standardised against alkaline copper solutions of known strength, due allowance being made for the variation in the titre of the solutions ocasioned by variation in bicarbonate concentration. The cyanide titration of these solutions is much sharper than in the case of ammoniacal copper solutions of equal copper content (*Analyst*, 1918, **43**, 268).

The carbonate and bicarbonate were determined by dilution of the solutions by means of carefully standardised pipette and flask, and titration by Winkler's method. A modification of this method

which proved serviceable consisted in running in $N/10$-sodium hydroxide solution until the bicarbonate was almost completely changed into carbonate, the amount necessary being found by a preliminary trial. Excess of neutral barium chloride solution and a drop of phenolphthalein were then added, and the titration with sodium hydroxide was completed. This modification is preferable in point of convenience to Winkler's method of adding excess of sodium hydroxide, then adding barium chloride and phenolphthalein, and titrating back, and appears to be quite as accurate, although, of course, several titrations of each solution must be carried out. If the quantity of sodium hydroxide solution first added is sufficiently near the quantity required for complete conversion (within 0·2 or $\overline{0}$·3 c.c.), there appears to be no difficulty occasioned by the decomposition of the barium bicarbonate which must be formed on adding barium chloride.

The following tables give the results of the several experiments made with the sodium copper solutions (table I) and with the potassium cobalt solutions (table II). No determinations of the cobalt content of the latter solutions are given, as sufficiently trustworthy values were not obtained at the time when the experiments were interrupted. The concentration of cobalt in the equilibrium solutions was in the neighbourhood of 0·1 to 0·2 gram per litre, and appeared to pass through a minimum value at a concentration of potassium carbonate equal to about 200 grams per litre. A similar variation is not found in the case of the sodium copper compound, with which the copper content of the equilibrium solutions increases continually with increase of the carbonate concentration.

TABLE I.

No. of experiment.	Hours stirring.	Solid phases.	Na_2CO_3 grams/litre.	$NaHCO_3$ grams/litre.	Cu grams/litre.
1	48	$Na_2Cu(CO_3)_2,3H_2O$ and $NaHCO_3$	9·27	87·79	—
2	140		11·08	86·45	0·0509
3	50		11·29	86·75	—
4	50		13·44	85·27	0·0542
5	50		37·36	78·63	—
6	100		61·32	74·18	—
7	100		62·36	72·65	0·0870
8	100		96·68	65·31	0·1061
9	50		99·30	64·10	0·1061
10	70		152·63	56·24	0·1411
11	50		168·75	53·60	0·1553
12	50	$Na_2Cu(CO_3)_2,3H_2O$ $NaHCO_3$ and $Na_2CO_3,10H_2O$	185·02	53·77	—
13	50	$Na_2Cu(CO_3)_2,3H_2O$ and $Na_2CO_3,10H_2O$	193·13	17·64	—
14	50		195·57	7·48	—
15	50		197·08	18·94	0·257

TABLE II.

No. of experiment.	Hours stirring.	Solid phases.	K_2CO_3 grams/litre.	$KHCO_3$ grams/litre.
1	120	$K_2Co(CO_3)_2,4H_2O$ and $KHCO_3$	13·3	280·6
2	70		14·85	282·5
3	50		25·5	272·4
4	240		47·5	262·3
5	100		103·2	237·0
6	70		114·1	230·7
7	40		125·1	227·6
8	50		145·7	219·0
9	120		166·8	203·2
10	120		220·0	181·0
11	120		289·4	158·9
12	70		309·2	151·3
13	40		453·5	108·4
14	70		607·7	68·9
15	120		643·0	64·1
16	120		704·3	54·6
17	120	$K_2Co(CO_3)_2,4H_2O$, $KHCO_3$ and $K_2CO_3,2KHCO_3,3H_2O$	800·2	43·1
18	120	$K_2Co(CO_3)_2,4H_2O$ and $K_2CO_3,2KHCO_3,3H_2O$	805·1	40·9
19	170		822·8	35·0
20	170	$K_2Co(CO_3)_2,4H_2O$, $K_2CO_3,2H_2O$ and $K_2CO_3,2KHCO_3,3H_2O$	825·8	33·1
21	100	$K_2Co(CO_3)_2,4H_2O$ and $K_2CO_3,2H_2O$	836·2	12·2
22	170		840·8	5·9

These results are represented graphically in Figs. 1 and 2. Fig. 1, which also contains McCoy and Test's results for the sodium carbonate–bicarbonate equilibrium at 25°, shows no sign of a break corresponding with the double compound $Na_2CO_3,NaHCO_3,2H_2O$ (trona) at 18°. It is therefore probable that this compound ceases to be stable in contact with solutions at some temperature between 18° and 25°.

In the course of the solubility experiments, it was noted that a distinct change in the appearance of the solid phase occurred in passing along the bicarbonate curve. The bicarbonate used in these experiments was the usual micro-crystalline variety, and this form appeared to suffer no change when left in the stirring bottle in contact with solutions ranging from pure bicarbonate to a point on the curve corresponding with about 70 grams of carbonate per litre. Beyond this point, the solid phase becomes transformed into well-formed, transparent crystals. These crystals are nevertheless pure anhydrous bicarbonate, as was established by repeated analyses. It is possible that a polymorphic change takes place, but in view of the fact that the solubility curve shows no break, and seeing that all attempts to obtain evidence of a definite transition point failed completely, the authors are inclined to think that the pheno-

menon is not to be explained by polymorphism. This opinion is supported by the absence of any clear distinction between the two

FIG. 1.

Upper curve, McCoy and Test, 25°
Lower „ Applebey and Lane, 18°.

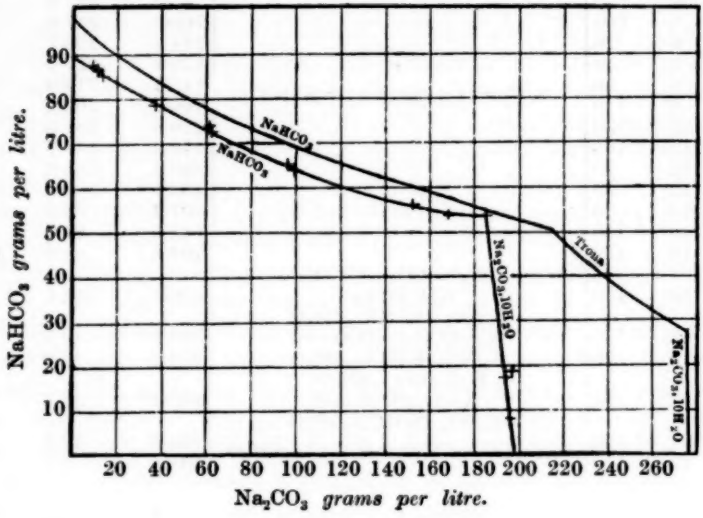
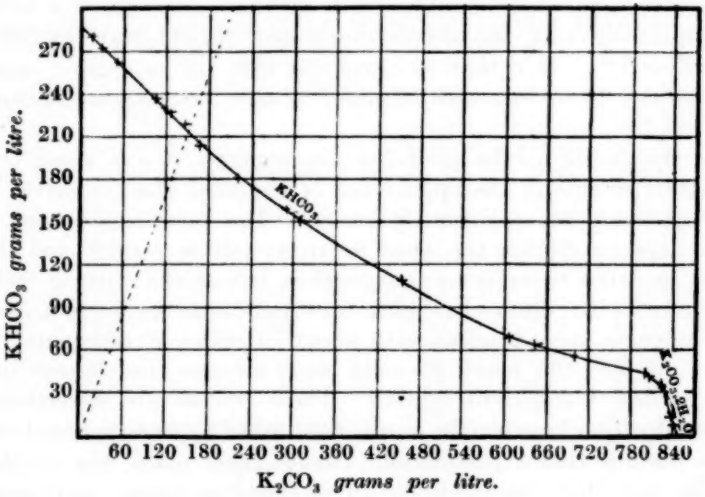


FIG. 2.



kinds of crystals when examined under the polarising microscope. Probably the conditions of the solubility equilibrium in presence

of considerable quantities of sodium carbonate are such as to facilitate the growth of the crystals.

Fig. 2, which is the corresponding diagram for potassium carbonate and bicarbonate, shows clear evidence of a double compound. This substance, the region of stability of which is very limited at 18°, is doubtless identical with the compound obtained by Bauer (*Ber.*, 1883, **16**, 1143) during the evaporation of bicarbonate solutions on a large scale in a mineral water factory. This salt was carefully analysed, and was examined crystallographically by Rammelsberg, but all attempts to obtain it synthetically have up to the present failed. Its formula is

$$K_2CO_3,2KHCO_3,3H_2O,$$

and, as the figure shows, it is only obtainable in equilibrium with a very limited range of solutions, which are very different in composition from the double salt itself.

The determinations of copper concentration in the equilibrium solutions lie on a smooth curve showing a steady increase with increase in the concentration of sodium carbonate. The copper determination of experiment 15 alone lies considerably above the curve. This point is the only determination of copper concentration in a solution in equilibrium with sodium carbonate decahydrate as solid phase, and seems to show that the rapid decrease in the bicarbonate concentration along the decahydrate curve brings about an increase in the copper content. Experiment 15 is, however, not very satisfactory, as the solution appears to have been somewhat supersaturated with carbonate owing to failure of the regulation of temperature, and the corresponding point lies at a considerable distance from the curve in Fig. 1 which connects the other points. The authors therefore content themselves with noting the observation, but lay no stress on its interpretation.

Discussion of Results.

The experimental results set forth above have several features of interest which throw some light on the nature of the equilibria involved. In the first place, it is noteworthy that the curve of copper concentrations does not approach the solubility of copper carbonate in water, which is negligibly small, as the concentration of sodium carbonate decreases, but the curves of solubility of copper carbonate and double salt appear to intersect at a copper concentration of about 0·045 gram per litre. This is unlike the normal case of double salt equilibrium in which the solubility of each component is lowered by the addition of the other. Assuming that this abnormal rise of solubility of copper carbonate in the presence

of sodium carbonate is due to the formation of the complex ion $Cu(CO_3)_2$, it is easily shown that the first effect of sodium carbonate must be to depress the solubility of the other component, the solubility passing through a minimum, and subsequently rising on addition of further quantities of the sodium salt. The investigation of this curve forms no part of the present investigations. It may be noted, however, as a point of interest, that by the application of the mass-action law, which is possibly justifiable in that only very dilute solutions are under consideration, it can be readily established that the position of the minimum solubility is given by the condition.

$$[Cu^{\cdot\cdot}]=[Cu(CO_3)_2''].$$

Passing now to the consideration of solutions saturated with the double salt, $Na_2Cu(CO_3)_2,4H_2O$, the results obtained in the present work are again at variance with the normal behaviour of double salts in that the increase of concentration of one component brings about an increase in the concentration of the other, the curve apparently rising throughout its whole course. This abnormal behaviour must, as in the case of the solubility of copper carbonate itself, be occasioned by the formation of a new constituent in the solution which removes copper from the solution equilibrium of the double salt, and so leads to an increase in its apparent solubility. The increasing solubility of the double salt with rising concentration of sodium carbonate thus constitutes a direct experimental proof of the view held by Deville that the copper in these solutions was largely present in some form chemically different from the salt which crystallises out.

Turning now to the identification of the dissolved substance, which is thus the parent of the crystalline double carbonate, a little consideration will show that if the substance is an ionisable one, the complex copper ion which forms the negative part must consist of a more heavily carbonated species, such as $Cu(CO_3)_4''''''$; the concentration of such an ion would increase with increasing concentration of carbonate. On the other hand, if such ions are present, it is very remarkable that double salts containing more than one equivalent of alkali carbonate to one of metallic carbonate never crystallise out of any of these alkali metallic carbonate solutions.

The authors are, however, of opinion that the true explanation of the solubility phenomena is to be found in the presence of a large proportion of the copper in the form of a colloidal substance, probably a normal or basic copper carbonate. This view accounts for the contrast between the colour of the solutions and that of the crystalline double salts, and is supported by the fact that

coagulation can certainly be brought about, although with difficulty, by the addition of much sodium phosphate to the solutions. The possibility that the solutions are of a colloidal nature has already been considered and rejected by Luther and Kršnjavi (*loc. cit.*) on the evidence of their transport experiments, and also because the solutions can diffuse through a parchment membrane. It appears, however, that such arguments, whilst they prove the presence of complex negative ions containing copper, do not at all exclude the simultaneous presence of a positive colloid, which may, in fact, be much greater in amount than the complex ions. In fact, it is obvious that when a solution contains a colloidal substance in kinetic equilibrium with crystalloids, the colloid will diffuse through an animal membrane by first changing into the dialysable form, the colloidal form being again obtained on the other side of the membrane by the reverse change. The passage of such a solute through a membrane will doubtless be slow in comparison with the rate of dialysis of crystalloids, but when the above conditions are fulfilled, such passage must take place. The escape of colloid normally comes to an end after a small quantity has passed, owing to the disappearance of some crystalloid factor on which the change to crystalloid form depends. An example which will make the argument clear may be found in ferric chloride. A solution of this substance may be regarded as made up of colloidal ferric hydroxide, ferric ions, and hydrogen and chlorine ions. In the dialyser, the ions, including the ferric ions, immediately begin to diffuse out, and diffusion of ferric ions will, in fact, continue as long as chlorine ions remain in the solution. The concentration of chlorine ions in such a solution is, however, not very great, and their escape is fairly rapid. The result is that escape of ferric ions soon comes to an end. In the case of the alkaline copper solutions, however, the crystalloid and diffusible substance, $Na_2Cu(CO_3)_2$, is constantly regenerated, since the solutions contain much sodium carbonate, which takes a considerable time to escape from the dialyser. The escape of copper is therefore more pronounced than that of iron from a ferric chloride solution, and, in fact, is so favoured by the presence of excess of sodium carbonate that the solution simulates the behaviour of a simple crystalloid.

It is perhaps worth noting that Luther and Kršnjavi remark that the movement of the coloured boundary in their transport experiments was very slow. This may to some extent be due to the conversion of the complex ions which have crossed the boundary into the positive colloid, which travels in the opposite direction by cataphoresis.

In conclusion, the authors wish to express their indebtedness to Mr. D. H. Nagel and to Mr. D. L. Chapman for much valuable assistance and advice during the progress of this work. They have also to thank Mr. S. G. Plant for assistance in carrying out some of the analytical work.

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LII.—*The Constitution of Carbamides. Part VI. The Mechanism of the Synthesis of Urea from Urethane.*

By Emil Alphonse Werner.

The formation of urea from the interaction of ammonia and urethane (ethyl carbamate) has always been considered to afford conclusive evidence in support of the 'carbamide' structure, and is commonly represented by the equation:

$$CO(OEt)_2 + 2NH_3 = CON_2H_4 + 2EtOH.$$

This synthesis of urea is invariably assumed to be analogous to the formation of acetamide from ethyl acetate, urethane being merely recognised as the normal intermediate product.

As a matter of fact, it is nothing of the kind.

When the true mechanism of the change is brought to light, it is seen to be nothing more than a modification of Wöhler's synthesis, namely, the formation of urea from the union of ammonia and cyanic acid in the keto-form.

Properties of Urethane, and the Conditions under which Urea is formed from the Ester.

The vapour density of urethane (b. p. 182°) at 202·8° (b. p. of *m*-cresol) was found to be 43·22, whilst theory requires 44·5; on the other hand, when the ester was boiled under reflux, it was gradually dissociated in accordance with the equation

$$EtO{\cdot}CO{\cdot}NH_2 \longrightarrow \underset{\text{(polymerised)}}{HCNO} + EtOH;$$

thus, after two hours, 16 per cent. of the theoretical yield of cyanuric acid was obtained.

The decomposition of the ester by alkali in aqueous solution was found to proceed on the same lines: the change is not a direct hydrolysis, as commonly stated in the literature, and may be represented thus:

(1) $EtO{\cdot}CO{\cdot}NH_2 + NaOH \longrightarrow H_2O + EtO{\cdot}C(ONa){:}NH \longrightarrow NaOCN + EtOH.$

(2) $NaOCN + 2H_2O = NaHCO_3 + NH_3.$

The following results were obtained when urethane and sodium hydroxide (both in $N/5$-solution) were heated at 100°:

Time in minutes.	Urethane decomposed, per cent.	Sodium cyanate formed, per cent.	Sodium carbonate formed, per cent.
5	50·9	32·9	18·0
15	62·5	37·25	25·25
30	63·95	29·70	34·25
60	66·80	28·80	38·0
90	71·0	17·0	54·0

At 15°, after three days, 18 per cent. of urethane was decomposed, with the formation of 5·5 per cent. of sodium cyanate and 12·5 per cent. of sodium carbonate. The change was therefore independent of dissociation of the ester (compare decomposition of urea, this vol., p. 88).

When urethane was heated in a current of hydrogen chloride, it was decomposed, thus:

$$EtO{\cdot}CO{\cdot}NH_2 + 2HCl = CO_2 + EtCl + NH_4Cl.$$

This decomposition of urethane in two different directions may be represented thus:

$$\underset{\text{(basic form)}}{EtO{\cdot}CO{\cdot}NH_2} \underset{\text{in presence of acid}}{\overset{\text{in presence of alkali}}{\rightleftharpoons}} \underset{\text{(acidic form)}}{EtO{\cdot}C(OH){:}NH.}$$

Since urea is formed from the hydrolysis of cyanic acid, thus,

$$2HCNO + H_2O = CON_2H_4 + CO_2$$

(this vol., p. 95), it is necessary to reach the temperature of the dissociation of urethane in solution in order to obtain urea from it; thus, when the ester was heated in aqueous solution in a sealed tube for two hours at 130°, 5·94 per cent. of the theoretical yield of urea was obtained; after six hours, the yield was 16·62 per cent. (Expts. II and III). Whilst the presence of ammonia would obviously promote the change, the origin of urea in this synthesis is clearly revealed by these results, and is properly represented thus:

$$CO\begin{cases}NH_2\\OEt\end{cases} \longrightarrow \begin{matrix}EtOH\\+\\HNCO\end{matrix} + NH_3 \longrightarrow HN{:}C\begin{cases}NH_2\\O\end{cases}.$$

A comparative study of the formation of urethane and ammonia from the interaction of urea and ethyl alcohol (a change which is also regarded from a false point of view) has brought to light evidence in support of the above explanations; thus, when a 5*N*-alcoholic solution of urea was heated for two hours at 150°, 41·66 per cent. of the theoretical yield of urethane was formed, as against 33·3 per cent. yield of urea from the interaction of urethane and ammonia under similar conditions (Expts. V and VI).

The greater facility with which urea dissociates explains the higher result in the former case, which otherwise appears abnormal, since the formation of an amide from an ester and ammonia takes place with ease, as compared with the reverse reaction.

Urea is a relatively stable substance, and if it has the 'carbamide' constitution, the question may be asked why it is not formed from ethyl carbonate (or carbamate) with the same ease as undoubted diamides are formed from esters and ammonia; for example, no urea was produced after urethane had remained in contact with a considerable excess of ammonia solution for ten months at the ordinary temperature.

It has been generally accepted as an axiom that the system $:C(OH)_2$ cannot form part of a stable molecule; the author now ventures to maintain that the evidence all round is no less convincing as regards the system $:C(NH_2)_2$, and herein lies the true answer to the question just stated. Urea, thiourea, and guanidine are the only known stable substances that have been assumed to contain this system, and in the case of thiourea it is well known that when the thiocarbamic esters $H_2N{\cdot}CS{\cdot}OEt$ and $H_2N{\cdot}CS{\cdot}SEt$ respectively are heated with ammonia in alcoholic solution, ammonium thiocyanate is formed. Since the reaction is effected below the temperature at which this salt dissociates (a necessary preliminary for the formation of the isomeride), no thiourea is produced, a fact for which no explanation can be offered when the erroneous 'thiocarbamide' structure is assumed.

As regards guanidine (free base), its constitution has yet to be proved (compare Krall, T., 1915, **107**, 1398).

Experimental.

The results of the decomposition of urethane by sodium hydroxide in aqueous solution were obtained as follows. A mixture of 0·89 gram of urethane, 10 c.c. of *N*-sodium hydroxide, and 40 c.c. of distilled water was heated to the boiling point under reflux for the stated periods. After the solution had been rapidly cooled,

the 'carbonate' was precipitated by barium nitrate and barium hydroxide; the filtrate, after careful neutralisation with dilute nitric acid, was precipitated with $N/10$-silver nitrate, the excess of which was titrated by Volhard's method. Each experiment was made in duplicate.

The results were calculated on the basis:

0·89 Gram of urethane $\longrightarrow$ $BaCO_3$ = 20 c.c. N-HCl.
NaOCN = 100 c.c. $N/10$-$AgNO_3$.

Example.—After one hour, $BaCO_3$ precipitated required for neutralisation 7·6 c.c. N-HCl, = 38·0 per cent. of the theoretical; NaOCN formed required for precipitation 28·8 c.c. $N/10$-$AgNO_3$, = 28·8 per cent. of the theoretical.

Decomposition of Urethane by Hydrochloric Acid.

Expt. I.—Twenty grams of urethane were heated to 150—160° in a distillation flask, while hydrogen chloride was passed through the liquid; after a short time crystals began to separate, and the heating was maintained for half an hour. The gas which was evolved (1) burned with a green flame (ethyl chloride), and (2) gave a copious precipitate with excess of barium hydroxide solution (carbon dioxide). The product was treated with ether to remove all unchanged urethane, and the residue, which was readily and completely soluble in cold water, contained Cl = 66·24 (NH_4Cl requires Cl = 66·35 per cent.), and gave no reaction for cyanuric acid.

The evolved gas, when collected over warm water, was reduced to almost half its volume after treatment with sodium hydroxide, and the residual gas burnt more freely than before with a green flame. The decomposition was therefore in accordance with the equation given.

Formation of Urea when Urethane was Heated with Water.

Expt. II.—2·5 Grams of urethane and 7·5 c.c. of water were heated in a sealed tube for two hours at 130°. After evaporation of the solution to dryness at 100°, the residue was extracted with ether, when there remained 0·05 gram, which was proved to be urea by the urease test and other reactions.

Expt. III.—As before, but the heating was maintained for six hours. Half of the final residue gave, when decomposed by

alkaline sodium hypobromite, 24·28 c.c. N_2 at *N.T.P.*, equal to 0·14 gram of urea, or 16·62 per cent. of the theoretical. Urea nitrate was readily prepared for identification from the remainder.

Formation of Ethyl Allophanate from Urethane.

Expt. IV.—A solution of 5 grams of urethane in 20 c.c. of alcohol was heated in a sealed tube for three hours at 150°. After evaporation of the alcohol, the residue was extracted with ether, and the insoluble product (0·065 gram) crystallised from hot water in colourless needles melting at 191°, which was the melting point of a specimen of ethyl allophanate used for comparison. When heated with barium hydroxide solution, a copious precipitate of barium carbonate was formed after a few moments, a reaction characteristic of the ester. Whilst the yield was small, the result proves that dissociation of urethane must have taken place.

Quantitative Comparison of (a) *Interaction of Urea and Alcohol*, (b) *Interaction of Urethane and Ammonia.*

Expt. V.—A solution of 3 grams of urea in 10 c.c. of alcohol (urea = 5*N*) was heated in a sealed tube for two hours at 150°; from the product, after evaporation of the alcohol and extraction with ether, 1·75 grams of urea were recovered, whilst 1·85 grams of urethane were obtained from the ethereal extract. As 3 grams of urea are equivalent to 4·45 grams of urethane, the yield of the latter was 41·6 per cent. of the theoretical.

Expt. VI.—A solution of 4·45 grams of urethane in 10 c.c. of alcohol (urethane = 5*N*) which contained 0·85 gram of ammonia was heated as in the last experiment. One gram of urea was obtained after extraction of the residue with ether. Hence the yield was equal to 33·3 per cent. of the theoretical.

A determination of the vapour density of urethane by V. Meyer's method at 202·8° gave the following result: 0·0763 gram gave 21·2 c.c. at 14·5° and 741·45 mm. (corrected), whence V.D. = 43·22. Hence there was no dissociation under this condition.

Summary.

(1) Urethane is not directly hydrolysed when heated with sodium hydroxide in aqueous solution, as commonly stated; alkali cyanate is first formed, and then hydrolysed.

(2) The formation of urea when urethane (or ethyl carbonate) is heated in solution with ammonia is solely dependent on the dissociation of urethane, and is no more than a repetition of Wöhler's synthesis in a modified form.

(3) A comparison of the reaction with the formation of urethane from urea and alcohol supplies evidence which is opposed to the 'carbamide' formula.

(4) Attention is directed to a rational inference from the facts, namely, that the system $:C(NH_2)_2$ cannot form part of a stable molecule.

The author desires to express his thanks to Miss M. Coade, B.Sc., for her assistance in conducting part of the experimental work.

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Trinity College, Dublin. [*Received, June 18th*, 1918.]

LIII.—*The Abnormality of Strong Electrolytes. Part II. The Electrical Conductivity of Non-aqueous Solutions.*

By Jnanendra Chandra Ghosh.

In a previous paper it has been shown that in aqueous solutions of strong electrolytes, the increase in molecular conductivity with dilution can be accounted for quantitatively on the basis of the following simple assumptions:

(*a*) Only ions exist in solution, the force of attraction between oppositely charged ions being governed by the law of inverse squares.

(*b*) In solutions of binary electrolytes, the arrangement of ions is analogous to the marshalling of atoms in a simple cubic crystal, whilst that of the ions in solutions of ternary electrolytes corresponds with the fluorspar lattice.

(*c*) The oppositely charged ions of a molecule form electrically saturated neutral doublets.

(*d*) It has been shown that, on the above hypothesis, the work necessary to separate the constituent ions of a gram-molecule of univalent binary electrolytes to an infinite distance,

$$A = \frac{NE^2 \sqrt[3]{2N}}{D\sqrt[3]{V}},$$

where N is Avogadro's number, E the charge on an ion, D the dielectric constant of the solvent, and V the molecular dilution. For a ternary electrolyte like barium chloride,

$$A = \frac{3NE^2 . 2 . \sqrt[3]{2N}}{D . \sqrt{3} . \sqrt[3]{V}}$$

(*e*) From Maxwell's equation of the distribution of velocities, it can be easily proved that the number of free ions in a solution containing a gram-molecule

$$= nN . e^{-\frac{A}{n . RT}}$$

where n is the number of ions into which a molecule dissociates.

(*f*) Since molecular conductivity is proportional to the number of free ions, and since $A = 0$ at infinite dilution,

$$\frac{\mu_v}{\mu_\infty} = \frac{n . N . e^{-\frac{A}{nRT}}}{nN} = e^{-\frac{A}{nRT}}$$

In this paper it will be shown that the above equation, which gives very good results in the case of aqueous solutions, can be applied with equal success to non-aqueous solutions of strong electrolytes.

The organic ionising solvents have been arranged by Walden in the following order: (1) alcohols, (2) aldehydes, (3) acids, (4) acid anhydrides, (5) acid chlorides, (6) esters, (7) acid amides and amines, (8) nitriles, (9) thiocyanates, (10) thiocarbimides, (11) nitro-compounds, (12) dimethylnitrosoamine, (13) ketones, (14) *epi*chlorohydrin (*Zeitsch. physikal. Chem.*, 1906, **54**, 130). This system of classification will be adhered to in the following pages.

1. *Alcohols.*

(a) *Methyl Alcohol.*—One of the most trustworthy investigations on the conductivity of electrolytes in methyl-alcoholic solutions is that of Carrara (*Gazzetta*, 1896, **26**, i, 119). The observed values of μ_v in tables I and II are taken from his work. The dielectric constant of methyl alcohol at 20° is 32·5. At 25° it is somewhat less; in the calculations, D has been taken as equal to 31. The solutes in tables I and II are all binary electrolytes, and μ_∞ is obtained from any particular value of μ_v by applying the equation

$$\frac{N . E^2 \sqrt[3]{2N}}{D . \sqrt[3]{V}} = 2RT \log_e \frac{\mu_\infty}{\mu_v} \quad . \quad . \quad . \quad . \quad . \quad (1)$$

This particular value of μ_∞ is afterwards utilised to calculate the molecular conductivity at other dilutions. It will be seen

from tables I and II that the agreement between the calculated and observed values of μ_v is very good, both in the case of the binary salts and the acids.

Carrara (*loc. cit.*) has also determined the molecular conductivities of strontium iodide in methyl alcohol at various dilutions. Here we expect the equation for ternary electrolytes:

$$\frac{3N.E^2.2.\sqrt[3]{2N}}{D.\sqrt{3}.\sqrt[3]{V}} = 3RT\log_e\frac{\mu_\infty}{\mu_v} \quad . \quad . \quad . \quad (2)$$

to hold good. Table III shows how well the calculated values agree with those observed.

TABLE I.

Solvent: Methyl alcohol. T = 25°.

Solute.	μ_∞ calc. from μ_{128}	v =	32.	64.	128.	256.	512.
1. NaI.....	94·0	μ_v calc.	68·9	73·5	77·3	80·5	83·0
		μ_v obs.	68·8	73·1	77·3	79·9	82·2
2. NaBr....	91·8	μ_v calc.	67·3	71·8	75·5	78·6	81·1
		μ_v obs.	65·8	71·0	75·5	79·9	82·8
3. NaCl ...	90·4	μ_v calc.	—	70·6	74·3	77·4	79·8
		μ_v obs.	—	69·6	74·3	78·1	81·8
4 KI	102·8	μ_v calc.	75·3	80·3	84·5	88·0	90·8
		μ_v obs.	73·8	79·5	84·5	88·5	91·0

TABLE II.

Solvent: Methyl alcohol. T = 25°

Solute.	μ_∞ calc. from	v =	18·9	37·7.	150·9.
HCl...	$\mu_{37\cdot7} = 157\cdot0$	μ_v calc.	108·4	117·0	130·4
		μ_v obs.	106·4	117·0	128·0
		v =	6·7.	26·8.	107·4.
HBr...	μ_∞ calc. from $\mu_{26\cdot8} = 142\cdot0$	μ_v calc.	84·0	101·9	115·0
		μ_v obs.	88·0	101·9	113·1
		v =	17·9.	71·4.	245·7.
HI ...	μ_∞ calc. from $\mu_{71\cdot4} = 152\cdot2$	μ_v calc.	104·4	120·0	130·0
		μ_v obs.	104·6	120·0	130·5

TABLE III.

Solvent: Methyl alcohol. T = 25°

Solute.	μ_∞ calc. from	v =	64.	128.	256.	512.
SrI_2...	$\mu_{128} = 200\cdot4$	μ_v calc.	114·6	128·6	141·0	151·2
		μ_v obs.	115·3	128·6	141·4	153·5

The most complete investigation in the field of non-aqueous solutions is that of Walden on solutions of tetraethylammonium iodide in various solvents. It is natural to expect that tetraethylammonium iodide would dissociate according to the following equation:

$$NEt_4I = NEt_4^{\cdot} + I'.$$

Except in the case of aldehydes, the variation of equivalent conductivity with dilution calculated from the equation for binary electrolytes (1) does not agree with the observed values. If, however, we assume that tetraethylammonium iodide at first undergoes polymerisation and then the double molecule $[NEt_4I]_2$ dissociates as a ternary electrolyte according to the equation:

$$[NEt_4I]_2 = 2NEt_4^{\cdot} + I_2''',$$

the calculated values of equivalent conductivities agree extremely well with the observed ones. Indeed, a cursory examination of the data on the variation of equivalent conductivity with dilution will at once lead to the conviction that the electrolytic dissociation of potassium iodide and tetraethylammonium iodide is not of the same type. If it were so, the variation of λ_v (equivalent conductivity) with dilution would have been of the same order. As a matter of fact, whilst λ_v for potassium iodide varies from 80·3 to 84·5 as the dilution increases from 64 to 128, the value for tetraethylammonium iodide increases by 8 units from 83·1 to 91·1 for the same change in dilution. Iodine has a great tendency to form complex ions. We are already acquainted with I_3', I_5' ions, etc. It is therefore not at all unreasonable to assume that in tetraethylammonium iodide solutions there exists a complex iodine ion of the type I_2''. Again, the consensus of opinion among electrochemists is generally in favour of complex molecules in non-aqueous solutions. The exact coincidence between the observed and calculated values of equivalent conductivity for tetraethylammonium iodide solutions, as shown in table IV, leaves no room for doubt as to the mode of dissociation of this salt in methyl-alcoholic solution. Of course, the above equation is equally applicable if the salt dissociates, thus:

$$[NEt_4I]_2 = [NEt_4]_2^{\cdot\cdot} + 2I'.$$

TABLE IV.

Solvent: Methyl alcohol. T = 25°.

Solute.	λ_∞ calc. from	V′ =	64.	127.	256.	512.	1024.
NEt_4I...	$\lambda_{128} = 130$	λ_v calc.	83·1	91·1	97·7	104·0	108·9
		λ_v obs.	82·1	91·1	98·0	103·6	108·6

In the above table V′ is the equivalent dilution.

(*b*) ***Ethyl Alcohol and Propyl Alcohol.***—The dielectric constant of ethyl alcohol at 20° is 21·7 (Walden, *loc. cit.*). In table V the observed values of molecular conductivity are taken from the work of Jones and Lindsay (*Amer. Chem. J.*, 1902, **28**, 341) (*loc. cit.*).

The conductivity of sodium iodide in propyl alcohol has been determined by Schlamp (*Zeitsch. physikal. Chem.*, 1894, **14**, 280). The dielectric constant of propyl alcohol, according to Rudolph, is 13·8.

TABLE V.

Solvent: Ethyl alcohol. T = 25°.

Solute.	μ_∞ calc. (equation 1) from	v =	64.	128.	256.	512.
KI.	$\mu_{256} = 44{\cdot}9$	μ_v calc.	31·6	33·9	36·0	38·5
		μ_v obs.	29·6	33·0	36·0	38·5

TABLE VI.

Solvent: Propyl alcohol. T = 25°.

Solute.	μ_∞ calc. (equation 1) from	v =	19·8.	55·4.	166·3.	500.
NaI.	$\mu_{166{\cdot}3} = 176{\cdot}0$	μ_v calc.	79·0	99·5	118·7	135·0
		μ_v obs.	77·0	97·1	118·7	138·0

2. *Aldehydes.*

Acetaldehyde, Propaldehyde, and Furfuraldehyde.—The dielectric constant of acetaldehyde is 21·2, according to Walden, and 18·6 according to Thwing. It is quite probable that the great reactivity of the solvent and its tendency towards polmerisation will completely prevent the formation of complexes in the solute. It is therefore to be expected that here at least tetraethylammonium iodide will dissociate normally as a binary electrolyte. The dielectric constant of propaldehyde is 14, whilst that of furfuraldehyde is 39·4.

TABLE VII.

Solvent: Acetaldehyde. T = 0°.

Solute.	μ_∞ calc. (equation 1) from	v =	100.	1000.	4000.
NEt_4I.	$\mu_{1000} = 178$	μ_v calc.	124·0	151·0	160·0
		μ_v obs.	122·0	151·0	158·0

TABLE VIII.

Solvent: Propaldehyde. T = 25°.

Solute.	μ_∞ calc. (equation 1) from	v =	100.	200.	400.	700.
NEt_4I.	$\mu_{200} = 127{\cdot}6$	μ_v calc.	81·0	89·0	95·8	101·8
		μ_v obs.	79·8	89·0	94·5	103·9

TABLE IX.

Solvent: Furfuraldehyde. T = 25°.

Solute.	μ_∞ calc. (equation 1) from	v =	200.	400.	800.	1600.
NEt_4I.	$\mu_{400} = 47{\cdot}8$	μ_v calc.	42·2	43·4	44·3	45·0
		μ_v obs.	41·6	43·4	45·0	45·8

3. *Acids.*

TABLE X.

Solvent: Thioacetic acid. T = 0°. D = 17·3.

Solute.	λ_∞ calc. (equation 2) from	V' =	320.	640.	1280.
NEt_4I.	$\lambda_{640} = 52{\cdot}5$	λ_v calc.	33·2	36·6	39·5
		λ_v obs.	32·7	36·6	40·2

4. *Acid Anhydrides.*

The dielectric constant of citraconic anhydride is 39. The agreement in this case is perfect.

TABLE XI.

Solvent: Citraconic anhydride. T = 25°.

Solute.	λ_∞ calc. (equation 2) from	V' =	100.	200.	400.	800.
NEt_4I	$\lambda_{200} = 24{\cdot}9$	λ_v calc.	18·5	19·7	20·7	21·5
		λ_v obs.	18·5	19·7	20·6	21·1

5. *Acid Chlorides and Bromides.*

In these solvents the agreement between the observed and calculated values of equivalent conductivity is always within the limits of experimental error, which is somewhat large.

6. *Esters.*

(*a*) *Organic Esters.*—The dielectric constant of methyl cyanoacetate is 28, and that of the ethyl ester is 26.

(*b*) *Inorganic Esters.*—Walden's data on the equivalent con-

ductivities of solutions of tetraethylammonium iodide in methyl sulphate, ethyl sulphate, and trimethyl borate are the most trustworthy. The dielectric constants are 46, 38, and 8 respectively. The agreement is always very good.

TABLE XII.

Solute: Tetraethylammonium iodide. T = 25°.

Solvent.	λ_∞ calc. (equation 2) from	V' =	100.	200.	500.	1000.	2000.
Methyl cyanoacetate.	$\lambda_{500} = 30{\cdot}8$	λ_v calc.	20·4	22·2	24·2	25·3	26·4
		λ_v obs.	20·3	22·1	24·2	25·3	26·1
Ethyl cyanoacetate	λ_∞ calc. (equation 2) from $\lambda_{500} = 28{\cdot}1$	λ_v calc.	17·9	19·7	21·6	22·8	23·8
		λ_v obs.	17·7	19·6	21·6	22·8	23·6

TABLE XIII.

Solvent: Methyl sulphate. T = 25°

Solute.	λ_∞ calc. (equation 2) from	V' =	200.	400.	800.	1600.	3200.
NEt_4I.	$\lambda_{400} = 44{\cdot}3$	λ_v calc.	36·1	37·7	38·9	39·9	40·7
		λ_v obs.	35·5	37·7	38·7	39·6	40·4

TABLE XIV.

Solvent: Ethyl sulphate. T = 25°.

Solute.	λ_∞ calc. (equation 2) from	V' =	200.	400.	800.	1600.
NEt_4I.	$\lambda_{400} = 40{\cdot}5$	λ_v calc.	31·9	33·5	34·9	36·0
		λ_v obs.	30·3	33·5	35·6	36·7

TABLE XV.

Solvent: Trimethyl borate. T = 25°.

Solute.	λ_∞ calc. (equation 2) from	V' =	200.	400.	800.
NEt_4I.	$\lambda_{400} = 32{\cdot}5$	λ_v calc.	10·2	13·0	15·7
		λ_v obs.	10·2	13·0	16·5

7. *Amides, Amines, etc.*

Among amides, formamide is a solvent that most resembles water. The inorganic salts dissolve in it quite as readily as in water, and, like the latter, it has a high dielectric constant, namely, 84.

Pyridine.—Laszczynski and Gorski have determined the conductivity of potassium iodide in pyridine solutions (*Zeitsch. Elektro-*

chem., 1897, **4**, 290), whilst Walden has determined the equivalent conductivity of tetraethylammonium iodide at various dilutions (*Zeitsch. physikal. Chem.*, 1906, **55**, 334). Acording to Schlundt, the dielectric constant of pyridine is 12·4 (*J. Physical Chem.*, 1901, **5**, 157, 503).

TABLE XVI.

Solvent: Formamide. T = 25°.

Solute.	λ_∞ calc. (equation 2) from	V' =	100.	200.	400.	800.
NEt_4I.	$\lambda_{200} = 29{\cdot}0$	λ_v calc.	25·2	26·0	26·5	27·0
		λ_v obs.	25·0	26·0	26·6	27·2

TABLE XVII.

Solvent: Pyridine. T = 25°.

Solute.	λ_∞ calc. (equation 2) from	V' =	100.	200.	400.	800.
NEt_4I.	$\lambda_{400} = 71{\cdot}0$	λ_v calc.	26·9	32·9	39·5	43·7
		λ_v obs.	27·0	33·0	39·5	46·0

	λ_∞ calc. (equation 2) from	V' =	178·5.	357·0.	714·0.
KI.	$\lambda_{714} = 50{\cdot}0$	λ_v calc.	22·8	26·9	30·7
		λ_v obs.	22·0	26·2	30·7

8. *Nitriles.*

The nitriles are excellent ionisers, and their dielectric constants are high. Thus glycollonitrile has a dielectric constant as high as 68, whilst the dielectric constants of acetonitrile, propionitrile, and benzonitrile are 37, 27, and 26 respectively.

TABLE XVIII.

Solvent: Acetonitrile. T = 25°.

Solute.	λ_∞ calc. (equation 2) from	V' =	200.	500.	1000.	2000.	4000.	8000.
NaI.	$\lambda_{500} = 199{\cdot}3$	λ_v calc.	155·0	165·9	172·3	177·4	182·0	185·4
		λ_v obs.	151·0	165·9	171·0	176·7	181·0	183·5

TABLE XIX.

Solvent: Propionitrile. T = 25°.

Solute.	λ_∞ calc. (equation 2) from	V' =	64.	128.	256.	512.	1024.
NEt_4I.	$\lambda_{128} = 169$	λ_v calc.	102·6	113·7	123·5	131·6	138·6
		λ_v obs.	102·0	113·7	123·4	131·5	139·4

TABLE XX.

Solvent: Benzonitrile. T = 25°.

Solute.	λ_∞ calc. (equation 2) from	V' =	200.	400.	800.	1600.
NEt_4I.	$\lambda_{400} = 55{\cdot}6$	λ_v calc.	39·0	42·0	44·5	46·6
		λ_v obs.	37·7	42·0	45·0	47·6

TABLE XXI.

Solvent: Glycollonitrile. T = 25°.

Solute.	λ_∞ calc. (equation 2) from	V' =	100.	200.	800.
NEt_4I.	$\lambda_{200} = 79{\cdot}5$	λ_v calc.	67·0	69·4	73·0
		λ_v obs.	66·8	69·4	71·0

TABLE XXII.

Solvent: Acetonitrile. T = 25°.

Solute.	μ_∞ calc. (equation 2) from	v =	100.	200.	400.
$CuBr_2$	$\mu_{200} = 73{\cdot}9$	μ_v calc.	49·8	54·0	57·7
		μ_v obs.	48·6	54·0	58·0

9, 10. *Thiocyanates and Thiocarbimides.*

The calculated values of equivalent conductivity also agree well with Walden's data for these solvents.

11, 12. *Nitro-compounds and Dimethylnitrosoamine.*

The dielectric constants of nitromethane and dimethylnitrosoamine are 39 and 53·3 respectively.

TABLE XXIII.

Solvent: Nitromethane. T = 25°.

Solute.	λ_∞ calc. (equation 2) from.	V' =	100.	200.	400.	800.	1600.
NEt_4I.	$\lambda_{200} = 127{\cdot}8$	λ_v calc.	94·5	100·5	105·4	109·6	113·0
		λ_v obs.	94·0	100·5	105·9	109·5	112·0

TABLE XXIV.

Solvent: Dimethylnitrosoamine. T = 25°.

Solute.	λ_∞ calc. (equation 2) from	V' =	250.	500.	1000.	2000.
NEt_4I.	$\lambda_{500} = 92{\cdot}0$	λ_v calc.	78·3	81·2	83·2	85·0
		λ_v obs.	77·5	81·2	84·2	86·4

13. *Ketones.*

The dielectric constant of acetone is 21, and that of acetylacetone is 22 at 25°.

TABLE XXV.

Solvent: Acetone. T = 25°.

Solute.	μ_∞ calc. (equation 1) from	v =	256.	512.	1024.
NaI	$\mu_{512} = 158{\cdot}5$	μ_v calc.	127·0	133·0	138·0
		μ_v obs.	126·3	133·0	139·0

TABLE XXVI.

Solvent: Acetylacetone. T = 25°.

Solute.	λ_∞ calc. (equation 2) from	V' =	200.	400.	800.	1600.
NEt_4I.	$\lambda_{400} = 86{\cdot}4$	λ_v calc.	56·9	62·0	66·4	70·0
		λ_v obs.	56·7	62·0	65·5	68·7

14. *Epichlorohydrin.*

TABLE XXVII.

Solvent: *epi*Chlorohydrin. T = 25°. D = 26.

Solute.	λ_∞ calc. (equation 2) from	V' =	100.	200.	400.	800.	1600.
NEt_4I.	$\lambda_{400} = 65{\cdot}7$	λ_v calc.	42·1	46·0	49·6	52·6	55·1
		λ_v obs.	40·0	45·0	49·6	53·7	56·8

Conclusion.

It will be seen that equations 1 and 2 have been subjected to a very severe test, and that their validity has been completely confirmed by the mass of experimental data on the conductivity of salt solutions in some thirty solvents.

The term "degree of dissociation" thus loses all significance in the case of strong electrolytes. In his first paper on the conduction of electricity by electrolytes, Arrhenius (*Bihang. der. Stockholmer. Akad.*, 1883, **8**, Nos. 13, 14) used the term "activity coefficient" for the ratio μ_v/μ_∞, and this is, indeed, a very suitable term in view of the fact successfully demonstrated here, that in salt solutions there are only free and bound ions. Incidentally, there has also been obtained a valuable method of determining the mode of dissociation of a solute in any solvent. Walden's normal electrolyte, tetraethylammonium iodide, really dissociates

abnormally. It is, however, the peculiar characteristic of this solute that the same type of dissociation persists in all the solvents. To this property are due the many regularities that Walden observed in tetraethylammonium iodide solutions. Thus we have his empirical law that "if solutions of one and the same normal electrolyte, tetraethylammonium iodide, in various solvents have the same degree of dissociation (activity coefficient), then for all solvents, the product of the dielectric constant, and the cube root of the dilution of that solution has always a constant value. Thus $D\sqrt[3]{V} = D'\sqrt[3]{V'}$, etc. $= k$, where D, D', etc., are the dielectric constants of the solvents, and V, V', etc., are the respective dilutions at which the activity-coefficient of tetraethylammonium iodide is the same. The theoretical significance of this general empirical law is at once brought out by equation 2. Since the mode of dissociation of the salt is always the same, the equation:

$$\frac{3N \cdot E^2 \cdot 2 \cdot \sqrt[3]{2N}}{D \cdot \sqrt{3}\sqrt[3]{V}} = 3RT \log_e \frac{\mu_\infty}{\mu_v}$$

is applicable to its solution in all solvents. For the same value of μ_v/μ_∞ it is obvious that

$$D\sqrt[3]{V} = k,$$

whatever be the nature of the solvent.

It was rightly suggested by Nernst and Thomson that the dielectric constant is the fundamental property which determines the dissociating power of a solvent. Walden's investigations proved conclusively that a direct parallelism exists between the dissociating power and the dielectric constants of solvents. The idea, however, never passed beyond the qualitative stage. In this paper, in the author's opinion, it has been proved beyond doubt that the exact quantitative relation between the activity-coefficient and the dielectric constant is given by equations 1 and 2.

Finally, it should be pointed out that the fundamental problem to be solved in this connexion is the work necessary to separate the constituent ions of a gram-molecule of a salt to an infinite distance at a given dilution. The assumption that the ions of a binary electrolyte are arranged according to a simple cubic lattice is necessarily arbitrary, although it is the simplest possible view. Some other views are possible, for example, we may have a face-centred cube lattice, a cube-centred lattice, etc. For ternary electrolytes good results have been obtained by assuming an arrangement corresponding with a fluorspar lattice. Here, also, it is possible that an ion, instead of occupying the centre of a cube, may be displaced diagonally towards an oppositely charged ion or towards an empty corner. Bragg has actually observed such dis-

placement in crystals of iron pyrites. It is therefore not necessary that the above rigid forms of equation should always be applicable. It ought to be always possible, however, to express the relation between the activity-coefficient, the dilution, and the dielectric constant of the solvent by equations of the above type. The behaviour of acetone solutions of ammonium iodide is a case in point. Equation 2 does not hold good in this case. If, however, we assume that the $NH_4^{\cdot}$ ions are displaced diagonally towards the oppositely charged I_2'' ion by one-fourth the length of the diagonal we get the following equation:

$$\frac{3N.E^2.4\sqrt[3]{2N}}{\sqrt{D}.\sqrt{3}.\sqrt[3]{V}} = 3RT\log_e\frac{\mu_\infty}{\mu_v}.$$

which holds good exactly as shown in table XXVIII.

TABLE XXVIII.

Solvent: Acetone.

Solute.	λ_∞ calc. from	V' =	128.	256.	512.	1024.	2048.
NH_4I.	$\lambda_{512} = 209$	λ_v calc.	69·0	86·9	104·1	120·2	135·0
		λ_v obs.	67·5	85·5	104·1	120·8	136·0

The above theory should not, therefore, be rejected in those cases where equations 1 and 2 do not hold good. We should rather proceed in the reverse direction, that is, calculate the total potential energy of the electrical doublets at a given dilution, from the observed value of the activity-coefficient at that dilution. An insight into the arrangement of ions in the interior of a solution will then be easily obtained, and the next problem will be to determine whether the equation based on this particular arrangement holds good at other dilutions. Theory demands that such should be the case, and it fails if the observed and the calculated activity-coefficients do not agree. In some cases, however, chemical action may interfere, as in the hydrolysis of salts, and these should be regarded as abnormal.

The fundamental hypothesis that only ions exist in salt solutions requires no elaborate justification in view of the fact conclusively established that even in a salt crystal there is no such thing as a molecule.

My best thanks are due to Prof. P. C. Rây, and to my friend and colleague, Mr. J. N. Mukherjee.

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LIV.—*A New Synthesis of Tetraphenylpyrrole.*

By GERTRUDE MAUD ROBINSON and ROBERT ROBINSON

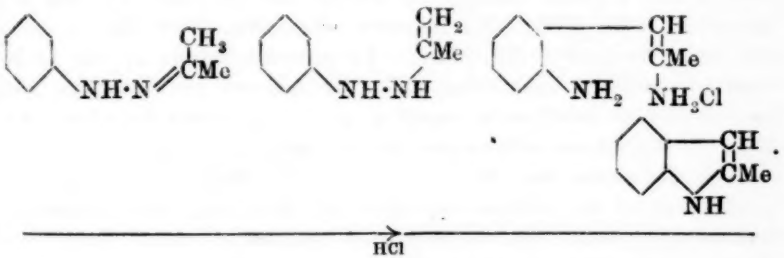
IN the course of an investigation having for its object the preparation of pyrrole, as a starting point for tropine, by an improved method, our attention was naturally directed to known methods of producing the pyrrole nucleus, among which E. Fischer's well-known synthesis of indole derivatives (*Annalen*, 1886, **236**, 126) occupies a prominent position. A necessary preliminary, however, to an attempt to apply an analogous process to the formation of true pyrroles seemed to be the formulation of a clear idea of the mechanism of the reactions involved in the decomposition of phenylhydrazones, and we have adopted a hypothesis which includes the following three stages:

(1) The transformation of the hydrazone into an unsaturated hydrazine, which is the isomeric change of an enimic into an enamic modification (compare J. F. Thorpe, P., 1909, **25**, 309). This is assumed to occur by the addition of the acid reagent and decomposition of the additive product.

(2) The benzidine-type rearrangement of the resulting hydrazine.

(3) Ring-formation by elimination of ammonium salt from the product, analogous to the formation of piperidine from the hydrochloride of pentamethylenediamine.

These changes are represented below in the case of the synthesis of 2-methylindole from the phenylhydrazone of acetone.



It will at once be recognised that the conditions necessary for the reaction, namely, an acid reagent and an elevated temperature, are those which would be expected to favour each of the above stages if considered separately, and in accordance with experience of molecular transformations due to the intervention of an acidic reagent it is noted that each stage is more basic than the last until, finally, the basic character is neutralised by the accident of

the formation of a ring of benzenoid character.* Thus a hydrazine is more basic than a hydrazone, and the hypothetical diamino-compound should be more basic still.

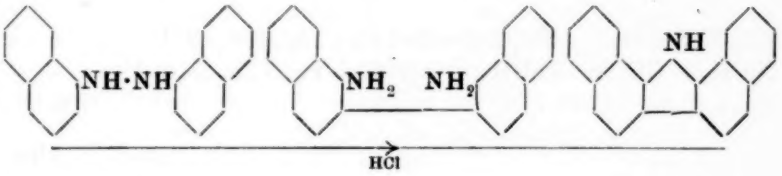
It seems probable that there is analogy between the enimic to enamic transformation and the ketone to enol change, and that the former would be likely to occur more easily in the cases of the hydrazones of those ketones which are readily changed to enols or enolic derivatives. The aldehydes and ketones, which are readily changed to enols, might therefore be expected to give phenylhydrazones readily convertible to indole derivatives if our hypothesis can be upheld. This is in accordance with experimental results, as the following examples show. Semmler (*Ber.*, 1909, **42**, 584) found that phenylacetaldehyde was converted into the acetate of the enolic modification by boiling with acetic anhydride, whereas acetophenone shows no such behaviour. Now Fischer and Schmitt (*Ber.*, 1888, **21**, 1072) showed that phenylacetaldehyde-phenylhydrazone was extremely easily transformed to phenylindole, and even by boiling with an alcoholic solution containing one-fifth of a molecular proportion of hydrochloric acid. On the other hand, acetophenonephenylhydrazone required heating with zinc chloride at 180° (Fischer, *loc. cit.*, p. 133). A similar comparison may be made between the cyclic ketones, such as *cyclo*hexanone and corresponding open-chain ketones. The former are well known to be more reactive than the latter in reactions which are assumed to depend on the enolic modification of the substances, and again the phenylhydrazones of the cyclic ketones are more readily transformed into indole derivatives than is the case with the phenylhydrazones of such ketones as diethyl ketone (compare Baeyer, *Annalen*, 1893, **278**, 106; Plancher, *Gazzetta*, 1898, **28**, ii, 387; Mannich, *Ber.*, 1906, **39**, 1594). In general, indoles appear to be readily produced from the phenylhydrazones of aldehydes and ketones which contain a negative group, particularly when this is in the β-position with respect to the carbonyl group.

It is interesting that Nef (*Annalen*, 1891, **266**, 71) observed the production of an indole derivative by dissolving ethyl β-phenylhydrazinocrotonate in concentrated sulphuric acid. This condensation product of phenylhydrazine and ethyl acetoacetate has

* The complete cyclic conjugation, which is probably the most characteristic feature of systems recognised as benzenoid, demands in the case of pyrrole a call on the latent valencies of the nitrogen atom. In pyridine, however, the latent valencies remain unaltered. It is possible, therefore, that a salt of pyridine retains its aromatic nucleus, whereas a salt of pyrrole cannot do so. Further, the latent valencies in pyrrole having been weakened, the preliminary dissociation necessary before salt-formation can take place is less likely to occur.

undoubtedly the unsaturated hydrazine structure, since it may be oxidised by mercuric oxide to an azo-compound previously obtained by Bender (*Ber.*, 1887, **26**, 2747), but under most conditions of condensation it merely loses alcohol with the formation of phenylmethylpyrazolone.

In the second phase of the reaction, an ortho-benzidine-type rearrangement has been assumed, and this may be realised in the case of certain naphthalene derivatives. Thus Nietzki and Goll (*Ber.*, 1885, **18**, 3252) obtained the isomeric diaminodinaphthyls, naphthidine and dinaphthyline, by the action of stannous chloride and hydrochloric acid on α-azonaphthalene, and, further, obtained a dinaphthacarbazole by boiling dinaphthyline with concentrated hydrochloric acid. Vesely (*Ber.*, 1905, **38**, 136) determined the constitution of the dinaphthacarbazole by an independent synthesis, so that the following changes are established:

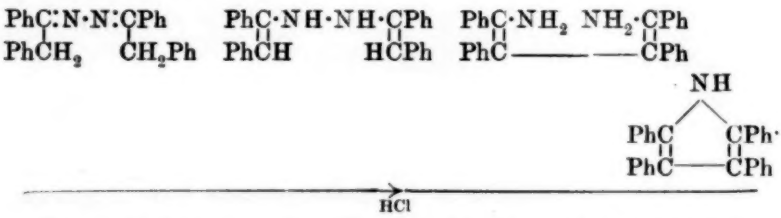


The similar formation of a dinaphthacarbazole from β-hydrazonaphthalene has been described by Meisenheimer and Witte (*Ber.*, 1903, **36**, 4161), and in these reactions we may perceive precise analogies to the second and the third stages of the synthesis of indoles from phenylhydrazones as postulated above.

Attention may also be directed to an interesting paper by Japp and Maitland (T., 1903, **83**, 267), who obtained carbazoles by heating phenols, such as β-naphthol, with arylhydrazines and their salts. These authors thought it probable that the phenol reacted in its tautomeric keto-modification with the production of a hydrazone, but even if this is the case, we are of the opinion that the next stage would be conversion to the hydrazine, bringing this part of the process into line with the formation of naphthylamine from naphthol by the action of ammonia, followed by reactions entirely similar to those involved in the two examples from the naphthalene series which are quoted above. The formation of a small quantity of *as*-1 : 2-dinaphthazine was observed by Japp and Maitland on heating β-naphthol with β-naphthylhydrazine and its hydrochloride. This could be explained as the result of a semidine transformation of β-hydrazonaphthalene followed by oxidation.

The application of the foregoing to the question of the possibility of synthesis of pyrrole derivatives by a corresponding method

seemed to be that divinylhydrazine and its derivatives should be convertible by acids into pyrrole and substituted pyrroles. Continuing this line of argument and reasoning from the first stage assumed above, it appeared not improbable that azines of substances containing the group $\cdot CH_2 \cdot CO \cdot$ might also, under correct conditions, be transformed into pyrroles. In this case, the initial tautomeric change is a double one and only likely to occur with facility in the molecules of azines of those ketones or aldehydes which show a marked tendency to change to related enols. To test our hypothesis, we chose what was regarded as one of the more favourable cases, namely, that of the azine of deoxybenzoin, and found that the action of dry hydrogen chloride on this substance at 180° converted it in almost a quantitative manner into the expected tetraphenylpyrrole and ammonium chloride. The reactions involved are represented below, in accordance with the views already discussed.



The scope of the reaction has not yet been defined, but in the case of the simpler aliphatic azines there is the competing transformation to pyrazolines, and we have been unable to obtain pyrrole from acetaldazine or dimethylpyrrole from dimethyl ketazine. The above explanation assumes what is perhaps a somewhat wider view of the benzidine transformation than is generally held, and in this connexion we have found the theory of partial dissociations serviceable.

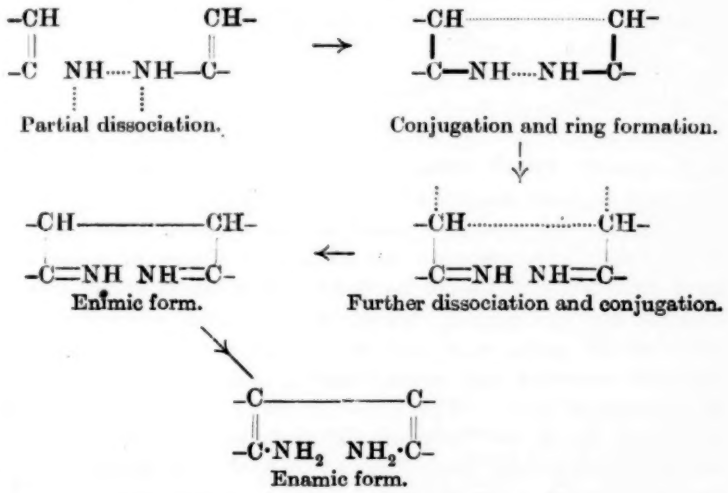
The following brief statement expresses the form in which this and related reactions may be generalised. In a molecular complex $A—b—c—D$, b or c or both represent atoms capable of assuming a higher valency by salt-formation. The salt absorbs energy and passes into an activated condition,* represented by $A—\overset{\vdots}{b}\cdots\overset{\vdots}{c}—D$

* The activated molecules are said to be 'partially dissociated' because the phenomenon appears to be a stage towards complete ionic dissociation, but the physical basis of the process is not quite clear. It may be that the energy change causes the movement of an electron from one atom to another (polarisation of the molecule) or a mere change in the position of one or more electrons within the sphere of the atom itself. In this case the evidence shows that the change is repeated in the same sense in alternate atoms

omitting the acid for reasons of convenience. If the partial valencies become conjugated with unsaturated groups in *A* or *D*, we obtain

$$A{=}b{\cdots}c{-}D \qquad \text{and} \qquad A{=}b{\cdots}c{=}D\,.$$

Ring-formation by the partial valencies followed by a second similar complete process leads in the first case to *b*—*A*—*c*—*D* and in the second to *b*—*A*—*D*—*c*. The products are obtained in the *keto-*, *enimic*, or *thioketo*-modifications, according as the atoms *b* or *c* are oxygen, nitrogen, or sulphur. The less extensive change is represented by the semidine transformation, the conversion of phenylhydrazine into *p*-phenylenediamine, of phenylnitroamine into nitroaniline, and by many other reactions. The full change resulting from conjugation of the partial valencies with both unsaturated groups *A* and *D* is represented by the benzidine rearrangement, and it is obvious that even within the four corners of the general scheme the nature of the products may be considerably varied according as the conjugated chains in *A* and *D* are long or short. The type of rearrangement assumed to occur in the synthesis of indole derivatives is represented below, and the thickened lines stand for a normal valency plus a partial valency.



forming part of a conjugated chain and in the opposite sense in the other atoms of the chain. Several further suggestions might be made, especially that a part use may be made of the field surrounding a single electron.

Experimental.

Preparation of Azines.

The processes described in the literature for the preparation of azines, and especially the ketazines, are far from convenient, and the employment of free hydrazine does not, in our experience, give such good results as that of a hydrazine salt and sodium acetate. The ketazines are readily obtained by the interaction of the calculated amounts of ketone and hydrazine sulphate in boiling aqueous alcohol in the presence of excess of sodium acetate. The yields correspond closely with those demanded by theory.

Phenyl benzyl ketazine was prepared by boiling a mixture of deoxybenzoin (6·3 grams), hydrazine sulphate (2·2 grams), sodium acetate (7 grams), water (60 c.c.), and alcohol (125 c.c.) during two hours under reflux. The product was collected and crystallised from ethyl acetate, and then melted at 164°, as stated by Curtius and Blumer (*J. pr. Chem.*, 1895, [ii], **52**, 137). This azine is quickly and completely hydrolysed by heating for a minute with alcohol and hydrochloric acid, and on the addition of water pure deoxybenzoin is precipitated. In view of the sparing solubility of the derivative, it may advantageously be employed for the otherwise rather troublesome purification of crude deoxybenzoin.

Tetraphenylpyrrole.

Evidence of the formation of tetraphenylpyrrole was obtained when phenyl benzyl ketazine was heated with zinc chloride, but the yield is much improved when dry hydrogen chloride is passed over the melted substance contained in a vessel heated at 180° in an oil-bath. The reaction was prolonged during an hour, and the solid product was found to consist of a mixture of ammonium chloride and the pyrrole derivative. The mass was extracted with sufficient hot acetic acid, and the crystals which separated on cooling were collected and washed with a little water to remove traces of ammonium salt. The yield of crude, dry tetraphenylpyrrole amounted to 88 per cent. of the theoretical. The substance was recrystallised several times from acetic acid, and obtained in colourless, flat needles melting at 214—215°. A specimen was prepared according to Garrett's method (*Ber.*, 1888, **21**, 3107), and found to melt at 214—215°, and a mixture of the two also melted at the same temperature.

The yellow solution in sulphuric acid becomes ivy-green on the addition of a trace of a nitrite or of a drop of nitric acid. In the

latter case, however, the liquid soon becomes brown, and on the addition of water a yellow nitro-derivative is precipitated. Acetaldazine and dimethyl ketazine were submitted to the action of dry hydrogen chloride, sulphanilic acid, and a number of other acid reagents and salts, such as zinc chloride, under varied conditions, but in all cases no pyrrole derivative was obtained, the only products being the corresponding pyrazoles and pyrazolines.

The formation of benzidine from hydrazobenzene has been discussed above, and a theory which has been occasionally advocated regards the transformation as passing through the intermediate stage of *p*-aminodiphenylamine. The method of preparation of this substance indicates its stability under conditions which favour the transformation of hydrazobenzene into benzidine, but to be more sure we prepared the compound by the usual process and endeavoured to convert it into benzidine, but without success. It was entirely unaffected by boiling with dilute or concentrated hydrochloric acid. 0·9 Gram of aminodiphenylamine was boiled during thirty minutes with 15 c.c. of concentrated hydrochloric acid; 0·82 gram of unaltered substance melting, after crystallisation from light petroleum, at 66—67° was recovered.

UNIVERSITY OF LIVERPOOL. [*Received, July 18th,* 1918.]

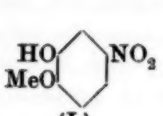
LV.—*Nitro-derivatives of Guaiacol.*

By FANNY POLLECOFF and ROBERT ROBINSON.

THE opinion has been expressed (Jones and Robinson, T., 1917, **111**, 906 *) that negative groups in the meta-position with respect

* In this paper the melting point of 6-bromoacetoveratrylamide was wrongly given owing to a clerical error (*loc. cit.*, p. 913). The melting point of this substance is 127°. In the same communication 6-nitroacetoveratrylamide melting at 199° and 6-nitroveratrylamine melting at 175° were described. Simonsen and Rau (this vol., p. 28) prepared the same substances and assigned to them the respective melting points 196° and 171°. A redetermination of the melting points of the specimens which had been preserved gave 199° for the acetyl derivative, whilst 6-nitroveratrylamine melted at 174·5°. The latter crystallises both in needles and in prisms. It is possible that the discrepancy is due to the fact that Jones and Robinson nitrated acetoveratrylamide in acetic acid solution, whilst Simonsen and Rau employed more concentrated nitric acid (D 1·4). Simonsen and Rau (*loc. cit.*) experienced difficulty in preparing veratrylamine unmixed with its chloro-derivative by the reduction of nitroveratrole with tin and hydrochloric acid, but were finally able to obtain a 50 per cent. yield by reducing at 100° with tin and hydrochloric acid in presence of graphite. We found that an

to a positive group exert an influence which is in the direction of favouring ortho-substitution with respect to the positive orientator. An example was found in the bromination of 5-nitroguaiacol (I), which yielded 6-bromo-5-nitroguaiacol (II), and we have now investigated the nitration of the same substance, and find that the main product is 5:6-dinitroguaiacol (III), mixed, however, with no inconsiderable proportion of 4:5-dinitroguaiacol (IV).



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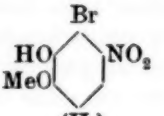

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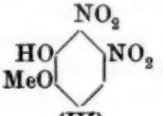
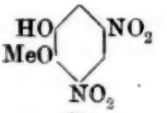


(III).

(IV.)



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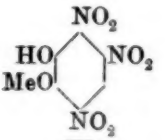

(VI.)

It was obviously interesting to extend the inquiry to the nitration of 3:5-dinitroguaiacol (V), in which there are two negative groups in the meta-position with respect to the phenolic hydroxyl. The desired substance was obtained by the nitration of guaiacol carbonate, which was changed first to a dinitro-derivative, the carbonate of 5-nitroguaiacol, and then to a tetranitro-derivative, which on hydrolysis yielded the new 3:5-dinitroguaiacol.

As was anticipated, the nitration of the latter resulted in 3:5:6-trinitroguaiacol (VI) as the sole product. The necessary proofs of constitution are obtained from the observations that the dinitroguaiacol from the tetranitro-derivative of guaiacol carbonate yields 4:6-dinitroveratrole on methylation, and that the methyl ether of the trinitroguaiacol is a new trinitroveratrole melting at 174°. The melting points of the known nitroguaiacols are tabulated below, in order to bring out the striking divergences which exist:

4-Nitroguaiacol, 101—102°.
5-Nitroguaiacol, 105°
6-Nitroguaiacol, 62°.

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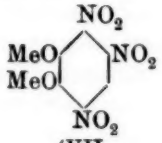
excellent yield could be obtained by shaking the nitroveratrole with tin, stannous chloride, hydrochloric acid, and some acetic acid in the cold until the reaction was complete. The amine was usually isolated as the acetyl derivative by eliminating the tin by the addition of zinc, and after rendering strongly alkaline with sodium hydroxide the solution was agitated with acetic anhydride. The crystalline precipitate of acetoveratrylamide was collected. Further quantities could be obtained by extraction of the alkaline solution with ether. R. R.

3-Nitroguaiacol is unknown.
3:5-Dinitroguaiacol, 80°.
3:5:6-Trinitroguaiacol, 129° (decomp.) 3:4:5-, 4:5:6-, and 3:4:6-trinitroguaiacols are unknown.
4:6-Dinitroguaiacol, 124°.
4:5-Dinitroguaiacol, 172°.
5:6-Dinitroguaiacol, 205—208° (decomp.).
3:5- and 3:4-Dinitroguaiacols are unknown.

3:5:6-Trinitroveratrole (VII) is changed by aqueous methyl-alcoholic ammonia into 3:5-dinitro-2:6-diaminoanisole (VIII), and by methyl-alcoholic sodium hydroxide into 4:6-dinitro-1:2:3-trimethoxybenzene (IX). The nitro-group displaced by ammonia is therefore that which is also displaceable by methoxyl, and in this respect the substance differs from the isomeric 3:4:5-trinitroveratrole, in which the nitro-group in position 4 is affected by ammonia, whilst that in position 5 is displaced by methoxyl when the trinitroveratrole is heated with a solution containing sodium methoxide.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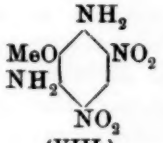
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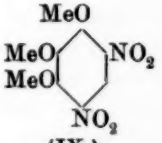

(IX.)

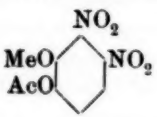
Experimental.

Preparation of 4-Nitroguaiacol.

Cardwell and Robinson (T., 1915, **107**, 255) prepared this substance by the hydrolysis of nitroveratrole by means of boiling aqueous methyl-alcoholic potassium hydroxide, but the yield was not quite satisfactory, and a certain amount of neutral material was recovered. It is now found that this consists partly of azoxyveratrole (compare G. M. Robinson, T., 1917, **111**, 109), and that if the methyl alcohol is omitted, the hydrolysis, although slow, proceeds practically quantitatively. The modified process constitutes by far the most convenient method available for the preparation of 4-nitroguaiacol. Nitroveratrole (5 grams) was boiled during thirty-six hours with a 10 per cent. aqueous solution (100 grams) of potassium hydroxide under reflux, and, on cooling, the potassium salt of the nitroguaiacol crystallised in golden-orange needles. Sufficient water to dissolve the salt was added, and on the addition of hydrochloric acid, 4-nitroguaiacol was precipitated in the crystalline condition, and was collected and dried in the air.

Nitration of 4-Nitroguaiacol and its Acetyl Derivative.

4-Nitroguaiacol was dissolved in nitric acid (D 1·42), when immediate reaction ensued, and, on the addition of water, a mass of needle-shaped crystals of 4:6-dinitroguaiacol was precipitated. The substance melted at 123° after crystallisation from alcohol, and gave a methyl ether melting after crystallisation at 101—102°. The yield closely approximated to that demanded by theory. 4-Nitroguaiacyl acetate is not affected by cold nitric acid (D 1·42), and although it is attacked by the fuming acid (D 1·5), the experiment is rather unsatisfactory, owing to the considerable loss which occurs through oxidation. The acetyl derivative was dissolved in ten times its weight of nitric acid (D 1·5), and the mixture cooled in running water at 15° during fifteen minutes. The product was poured into water, when the oil soon solidified, and after collection, washing, and drying, weighed approximately half as much as the material employed. Repeated crystallisations from methyl alcohol resulted in the isolation of unchanged 4-nitroguaiacyl acetate, but, after hydrolysing the acetyl derivatives contained in the mother liquors by the addition of dilute aqueous potassium hydroxide and gently heating the solution, a precipitate of 4:5-dinitroguaiacol (see below) was obtained on acidification. When the nitration was carried out during only two minutes, much unchanged material was recovered, and the methyl-alcoholic mother liquors were in this case treated with potassium hydroxide and methyl sulphate in large excess; the resulting methyl ethers on repeated crystallisation from methyl alcohol yielded pure 3:4-dinitroveratrole melting at 91°. The nitration of 4-nitroguaiacyl acetate, therefore, results in the production of the compounds



and

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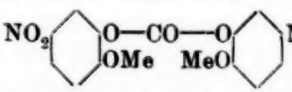
in undetermined proportions, and the loss on continued nitration appears to be due to the destruction of the first of these by oxidation.

5-Nitro-2-methoxyphenyl Carbonate,



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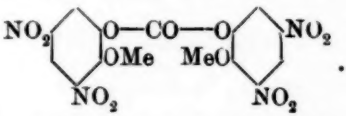
Guaiacol carbonate (10 grams) was finely powdered and added in one portion to nitric acid (100 c.c., D 1·42), mechanically stirred,

and cooled to 0°. These conditions were maintained during three hours; water was then added, and the nearly colourless product collected and well washed with water. The yield is excellent and the material sufficiently pure for further experiments, especially if it be extracted with a little warm alcohol. The substance crystallises from methyl alcohol in colourless needles melting at 133°, and moderately sparingly soluble in the usual solvents:

0·1663 gave 0·2999 CO_2 and 0·0510 H_2O. C = 49·2; H = 3·4.
$C_{15}H_{12}O_9N_2$ requires C = 49·5; H = 3·3 per cent.

The substance yields 5-nitroguaiacol on hydrolysis, and is a convenient source of the latter. The carbonate (4 grams) was heated on the steam-bath with a solution of sodium hydroxide (3 grams) in water (60 c.c.) until a clear solution was obtained on dilution with water. On acidification with hydrochloric acid, pure 5-nitroguaiacol was obtained in needles.

3:5-*Dinitro-2-methoxyphenyl Carbonate*,



The foregoing carbonate of 5-nitroguaiacol (3 grams) was dissolved in nitric acid (20 c.c., D 1·5), and the solution allowed to remain at the ordinary temperature during four hours. A certain proportion of the tetranitro-derivative separated in needles and the remainder was precipitated on the addition of water. The yield was almost that demanded by theory. The substance separated from benzene in short, colourless needles melting at 148°:

0·2113 gave 0·3050 CO_2 and 0·0403 H_2O. C = 39·4; H = 2·1.
$C_{15}H_{10}O_{13}N_4$ requires C = 39·6; H = 2·2 per cent.

This compound is readily soluble in ethyl acetate, sparingly so in ether or alcohol, and moderately so in benzene. There was no evidence of the formation of isomeric nitro-derivatives in the two stages of the nitration of guaiacol carbonate.

3:5-*Dinitroguaiacol* (V).

The carbonate (20 grams) described in the last section was heated on the steam-bath with sodium carbonate (50 c.c. of saturated aqueous solution), water (100 c.c.), and alcohol (30 c.c.) until a homogeneous solution resulted. After cooling, the nitrophenol was precipitated by the addition of hydrochloric acid, collected, washed

with water, and dried (18·5 grams). The substance was readily soluble in alcohol or ethyl acetate, more sparingly so in benzene, chloroform, or carbon disulphide. It was crystallised from toluene and then from carbon disulphide, and obtained in pale yellow needles melting at 80°:

0·2948 gave 0·4203 CO_2 and 0·0699 H_2O. C = 39·0; H = 2·6.
$C_7H_6O_6N_2$ requires C = 39·2; H = 2·8 per cent.

This dinitroguaiacol dissolves readily in aqueous sodium carbonate to a yellow solution, and the sodium salt is obtained in glistening, orange needles by the addition of sodium hydroxide. Not containing a nitro-group in the ortho- or para-position with respect to the hydroxyl group, this substance may be comparatively readily methylated in alcoholic solution by means of methyl sulphate and potassium hydroxide, but even in this case it was found more convenient to employ the xylene–methyl sulphate–sodium carbonate method. The methyl ether was identified with 3:5-(or 4:6-)-dinitroveratrole, melting after crystallisation from alcohol at 102°.

5:6-*Dinitroguaiacol* (III).

5-Nitroguaiacol (15 grams) in acetic acid (50 c.c.) was nitrated by the addition of nitric acid (20 c.c., D 1·42), diluted with acetic acid (10 c.c.) with constant stirring, and cooling in running water. The first half of the acid mixture was added during five minutes and the second portion during one minute. Water was then added immediately, and the product collected, washed, and dried (14·7 grams). This was dissolved in hot ethyl acetate (65 c.c.), and, on cooling, 4·8 grams of well-defined yellow prisms were deposited. The mother liquor was mixed with an equal volume of benzene, and this induced no further separation, but, on the addition of 100 c.c. of light petroleum, 2·5 grams gradually crystallised. This material was a mixture, and by further treatment with ethyl acetate and light petroleum ultimately yielded 2·2 grams of the yellow prisms. A further 0·1 gram was obtained from the mother liquors after separation of the 4:5-isomeride (see below), so that the total yield was 7·1 grams. The substance so isolated was practically pure 5:6-dinitroguaiacol, and it was crystallised, first from ethyl acetate and then again from toluene, and obtained in pale yellow prisms which became orange at about 200° and began to melt at 205°, with vigorous decomposition near 208°:

0·1071 gave 0·1547 CO_2 and 0·0280 H_2O. C = 39·4; H = 2·9.
$C_7H_6O_6N_2$ requires C = 39·2; H = 2·8 per cent.

This substance is more sparingly soluble in most organic solvents

than any of the isomerides which we have examined. It dissolves in aqueous sodium carbonate, and, on the addition of concentrated sodium hydroxide, an orange salt is precipitated in shining needles.

The *acetyl* derivative is obtained by heating the nitrophenol with acetic anhydride, and crystallises from alcohol, in which it is somewhat sparingly soluble in the cold, in slender, pointed, colourless needles melting at 124—125°.

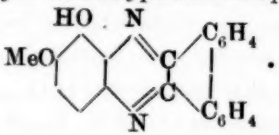
The *methyl ether* is identical with 3:4-dinitroveratrole, and was prepared by methylation with methyl sulphate and sodium carbonate in boiling xylene solution. The residue from the removal of the solvent in a current of steam was collected and crystallised many times from methyl alcohol, and obtained in flat needles melting at 91°:

0·1158 gave 0·1784 CO_2 and 0·0383 H_2O. C=42·0; H=3·7.

$C_8H_8O_6N_2$ requires C=42·1; H=3·5 per cent.

Jones and Robinson (T., 1917, **111**, 911) obtained a product melting at 96°, with previous softening, by the nitration of 3-nitroveratrole, and this was shown to contain 3:4-dinitroveratrole, because, after reduction and condensation with phenanthraquinone, 1:2-dimethoxyphenanthraphenazine (Pisovschi, *Ber.*, 1910, **43**, 2137) was obtained. It was pointed out at the time that the product was obviously impure, and it now appears that it must have contained 4:5-dinitroveratrole, owing to the presence of 4-nitroveratrole in the 3-nitroveratrole, which was the starting point, and we have therefore repeated the experiment with carefully purified 3-nitroveratrole, and have obtained a product melting at 91° and identical with that described above.

1-*Hydroxy*-2-*methoxyphenanthraphenazine*,



5:6-Dinitroguaiacol was reduced by the addition of zinc dust in excess to its solution in aqueous alcoholic hydrochloric acid, and the filtered solution, mixed with sodium acetate, was then heated with phenanthraquinone dissolved in hot aqueous sodium hydrogen sulphite. The precipitated phenazine derivative was collected and washed with alcohol, after which it was crystallised from acetic acid, and again by adding alcohol to its solution in nitrobenzene. It was obtained in glistening, golden-yellow needles melting at 224°, and dissolving in sulphuric acid to a rose-red solution:

0·0961 gave 0·2715 CO_2 and 0·0418 H_2O. C = 77·5; H = 4·7.
$C_{21}H_{14}O_2N_2$ requires C = 77·3; H = 4·3 per cent.

In alcoholic suspension, the substance was converted by sodium hydroxide into a dull mauve-red sodium salt, which reacted very readily with methyl sulphate with the production of 1:2-dimethoxyphenanthraphenazine (Pisovschi, *loc. cit.*), melting after crystallisation from alcohol at 175°. The curious colour of this sodium derivative appeared to be characteristic of the substance, and persists in the microscopic threads which separate from hot alcoholic solutions of the compound.

4:5-*Dinitroguaiacol* (IV).

The ethyl acetate–benzene–light petroleum mother liquor from the crystallisation of 5:6-dinitroguaiacol in the preparation described above (starting with 15 grams of 5-nitroguaiacol) was shaken with dilute sodium hydroxide, and the separated aqueous solution acidified with hydrochloric acid. The recovered nitrophenols were collected and found to consist chiefly of 4:5-dinitroguaiacol. The material was crystallised from a litre of boiling water, and obtained in long, yellow needles, and then again from toluene. The aqueous mother liquor was rendered alkaline and used to wash the toluene mother liquors, after which the solution was acidified and extracted with ether. The residue, after evaporation, was submitted to treatment with ethyl acetate, and, as already stated, some 5:6-dinitroguaiacol was isolated. Altogether, 5·7 grams of the 4:5-isomeride were obtained. The substance crystallised in long, pale yellow needles melting, when quite pure, at 172°, but many crystallisations are necessary in order to reach this value, and apparently pure material melted at 163—165°. The purest specimen was obtained by crystallisation from water followed by recrystallisation from alcohol and from xylene:

0·1439 gave 0·2045 CO_2 and 0·0350 H_2O. C = 38·8; H = 2·8.
$C_7H_6O_6N_2$ requires C = 39·2; H = 2·8 per cent.

The *acetyl* derivative crystallises from methyl alcohol in colourless, prismatic needles which sinter at 114° and melt at 123—124°. It is sparingly soluble in cold methyl alcohol.

The *methyl ether*, obtained in the usual way, was identified with 4:5-dinitroveratrole.

2-*Hydroxy*-3-*methoxyphenanthraphenazine* was obtained from 4:5-dinitroguaiacol in the manner described above for the preparation of an analogous substance from 5:6-dinitroguaiacol. It crystallised best from carbon disulphide in silky, yellow threads

melting at 239—240°, and dissolving in sulphuric acid to a rich magenta solution.

3:5:6-*Trinitroguaiacol* (VI).

It was not found practicable further to nitrate 4:6-, 5:6-, or 4:5-dinitroguaiacol, but the 3:5-isomeride was readily converted into a trinitroguaiacol. 3:5-Dinitroguaiacol (40 grams) was dissolved in nitric acid (200 c.c., D 1·42), and any rise of temperature was checked by cooling in running water. After half an hour, a certain amount of the product had crystallised from the solution, and water (300 c.c.) was added and as much salt as would dissolve in the solution. The precipitate was collected, washed with a little brine, and then with the minimum of dilute hydrochloric acid, and dried in the air (38 grams). The substance crystallised from benzene in needles containing solvent of crystallisation, and from chloroform in yellow prisms, which melt at 129° with vigorous decomposition, and evolution of much gas at a slightly higher temperature. This decomposition is not accompanied by charring, and is apparently a smooth process resulting in definite products. When the substance was heated quite gently in a test-tube, there was a mild explosion and the production of relatively much hydrocyanic acid was observed. In combustions, a low result was always obtained for carbon, but the composition of the substance is fixed by other experiments, which are described below. The substance dissolves in water to an intensely yellow solution resembling in appearance a solution of potassium chromate, and on the addition of hydrochloric acid the colour changes to that of a dilute solution of picric acid, and the substance crystallises in prisms. Silk and wool are dyed from aqueous solutions, the former in greenish-yellow and the latter in orange-yellow shades. The trinitroguaiacol also resembles picric acid in forming sparingly soluble salts with bases, and it may be employed as an alkaloidal precipitant.

Attempts were made to compare its molecular weight with that of picric acid by titration of both nitrophenols with a solution of a basic dye, with which each compound forms a sufficiently sparingly soluble salt. After a number of trials, it was found that Rhodamine 6G gave satisfactory results. The method was the following. The nitrophenol solution was mixed with salt and a solution * of Rhodamine 6G containing approximately 1 gram in 500 c.c. of water gradually added with constant stirring to ensure formation of the additive product and in order to avoid premature salting out of the dye. When the supernatant liquid appeared to

* It was unnecessary to ascertain the exact strength of the solution.

have a slight fluorescence, the end-point was near, but not reached until a filtered portion of the solution had a faint pink colour. The reason for this is that when the concentration of nitrophenol is low, the rhodamine salt appears to be just sufficiently soluble to exhibit fluorescence in solution. It was found best to make a rough experiment first, and to repeat it in order to obtain the exact result:

0·2386 Gram of picric acid dissolved in water and made up to 250 c.c.

25 c.c. with 20 grams of salt required 56·2 c.c. of Rhodamine 6G solution.

0·2255 Gram of trinitroguaiacol dissolved in water and made up to 250 c.c.

25 c.c. with 20 grams of salt required 59·9 c.c. of Rhodamine 6G solution.

Whence, assuming equivalence of picric acid and trinitroguaiacol in regard to rhodamine base, M.W. = 258.

$C_7H_5O_8N_3$ requires M.W. = 259.

Pyridine Salt.—This highly characteristic derivative separates in slender, canary-yellow needles when a drop of pyridine is added to a dilute aqueous solution of trinitroguaiacol. It crystallises from methyl alcohol in long, yellow needles melting at 194—195° when quickly heated, but if slowly heated, the melting point may be found as low as 180°, or more usually in the neighbourhood of 185°. This behaviour is due to the decomposition which accompanies the melting, and is apparently slow at 180°. As the substance is very readily prepared and purified, it was used to prove that 3:5:6-trinitroguaiacol is the only product of the nitration of 3:5-dinitroguaiacol, and in this case the specimens were always compared by simultaneous heating:

0·2257 gave 0·3549 CO_2 and 0·0561 H_2O. C = 42·9; H = 2·8.

$C_7H_5O_8N_3,C_5H_5N$ requires C = 42·8; H = 3·0 per cent.

This derivative was isolated from the mother liquors from the crystallisation of 3:5:6-trinitroguaiacol, and also from the original nitric acid solution from which the crude product was separated. It was useful as a means of isolating the trinitroguaiacol from aqueous solution, and could be employed directly for the preparation of the trinitroveratrole described below.

3:5:6-*Trinitroveratrole* (VII).

This ether was readily obtained by the methylation of trinitroguaiacol or its pyridine salt by means of methyl sulphate and

sodium carbonate in boiling xylene solution. Care was taken to ensure reaction between the phenol and sodium carbonate before raising the mixture to the boiling point, since, although the sodium salt is comparatively stable, the free trinitroguaiacol undergoes decomposition in boiling xylene solution. Also, hot aqueous sodium carbonate has some action on the trinitroveratrole, and the xylene solution is accordingly poured away from the excess of sodium carbonate after the reaction, and then submitted to distillation in a current of steam. The pale brown powder which remains in the flask when the solvent has been removed is collected and crystallised from acetic acid, and then from alcohol. The substance is obtained in very pale yellow needles melting at 174°, and sparingly soluble in alcohol, acetic acid, or chloroform, but readily so in ethyl acetate or acetone. The solution in the latter solvent is yellow, and becomes orange on the addition of a drop of ammonia:

0·1317 gave 0·1710 CO_2 and 0·0335 H_2O. C = 35·4; H = 2·8.

$C_8H_7O_8N_3$ requires C = 35·1; H = 2·6 per cent.

The substance is sensitive to alkalis, and is decomposed slowly by cold aqueous sodium hydroxide and by boiling aqueous sodium carbonate. It reacts with primary and secondary bases with elimination of a nitro-group, but the products were not closely examined. On boiling with a concentrated solution of sodium sulphite, the substance is attacked, and in this and other respects it exhibits greater reactivity than the isomeric 3:4:5-trinitroveratrole. On the addition of salt to the resulting yellow solution, a pale yellow substance separated in flat needles, and this material had the properties that would be associated with the expected product, namely, *sodium* 3:5-*dinitroveratrole*-6-*sulphonate*.

3:5-*Dinitro*-2:6-*diaminoanisole* (VIII).

This substance was readily prepared by boiling 3:5:6-trinitroveratrole with an excess of methyl-alcoholic aqueous ammonia under reflux for half an hour. The red product crystallised from the hot solution, and, after cooling, was collected and several times crystallised from ethyl acetate. It is obtained in garnet needles which soften at 225° and melt at 237°, and is sparingly soluble in most organic solvents. In general character it resembles the isomeride which is obtained from 3:4:5-trinitroveratrole:

0·0981 gave 0·1331 CO_2 and 0·0319 H_2O. C = 37·0; H = 3·6.

$C_7H_8O_5N_4$ requires C = 36·8; H = 3·5 per cent.

The substance is devoid of basic character, and on boiling with dilute aqueous sodium hydroxide, ammonia is evolved and a corre-

sponding nitrophenol obtained. On acidifying the solution, the latter is precipitated in orange-yellow, flat needles.

4:6-*Dinitro*-1:2:3-*trimethoxybenzene* (IX).

3:5:6-Trinitroveratrole yielded a bright orange-red solution on the addition of powdered potassium hydroxide to its suspension in methyl alcohol, and, on boiling, the colour gradually faded, and finally a yellow solution was obtained. On the addition of water, an oil separated, and after a short time this crystallised and was collected. The aqueous solution was proved to contain a nitrite. The substance was readily soluble in most organic solvents, but sufficiently sparingly so in methyl alcohol for purposes of crystallisation. It was obtained in pale yellow needles melting at 85°:

0·1262 gave 0·1936 CO_2 and 0·0462 H_2O. C = 41·8; H = 4·1.

$C_9H_{10}O_7N_2$ requires C = 41·9; H = 3·9 per cent.

The constitution of this compound follows from its conversion by heating during three days in a sealed tube at 100° with methyl-alcoholic ammonia into the dinitrodiaminoanisole described above, and confirmation is found in the observation that on reduction a diamine is produced which does not condense with phenanthraquinone to a derivative of phenazine.

UNIVERSITY OF LIVERPOOL. [*Received, July 18th*, 1918.]

LVI.—*The Propagation of Flame through Tubes of Small Diameter.*

By WILLIAM PAYMAN and RICHARD VERNON WHEELER.

IT has been shown in a previous communication (T., 1917, **111**, 1044) that the speed of the "uniform movement" of flame in a given mixture of methane and air is dependent on the diameter of the tube along which the flame travels, being enhanced by the action of convection currents in tubes of large diameter and reduced by conduction of heat by the walls in tubes of small diameter.

If the diameter of the tube is sufficiently small, the "uniform movement" of flame does not develop, but the flame dies out after travelling a few centimetres. Still further reduction in the diameter of the tube renders it impossible for the flame to spread

any measurable distance from the point of ignition. This fact was discovered by Davy, and was the starting point of his researches on the construction of a safe lamp for use in coal mines, his observation being: "I found that in tubes of 1/7-inch in diameter explosive mixtures"—of firedamp and air—"could not be fired when they were opened in the atmosphere" ("Collected Works," Vol. 6, p. 11).

Schloësing and de Mondésir (quoted by St. Claire Deville, "Leçon sur la Dissociation," p. 46) and Mallard and Le Chatelier (*Ann. des Mines*, 1883, [viii], **4**, 319) experimented on this subject, and the last-named have placed on record the speeds of flame in a mixture of methane and air containing 10·4 per cent. of methane, using tubes of glass of different diameters, as follow:

Diameter of tube, mm.	3·2	5·5	8·0	9·5	12·2
Speed of flame, cm. per sec....	nil	22	39	41	47

The methane used by Mallard and Le Chatelier was prepared from sodium acetate, and was impure; nevertheless, their observation that flame would not propagate in glass tubes of 3·2 mm. internal diameter is in fair agreement with Davy's statement (one-seventh of an inch is equal to 3·63 mm.).

Following on his discovery that a tube of small diameter would not allow flame to pass through it, Davy experimented with other means of exposing a cooling surface to the flame, such as perforated plates and systems of concentric tubes, and finally produced his wire gauze safety-lamp. A history of the development of the miners' flame lamp from Davy's original design would be out of place here, but it may be said that the retention of the wire gauze to protect the oil- or spirit-flame from inflammable mixtures of firedamp and air seems to have been regarded as essential by the majority of inventors. A few types of lamps have been constructed in which metal plates perforated with fine holes have been used, but no systematic experiments seem to have been recorded, on the lines of Davy's earlier experiments, to determine under what conditions tubes or perforated plates can be regarded as equivalent in safety to the gauze adopted, mainly for its convenience, by Davy.

In connexion with work on the construction of miners' safety-lamps, we have made a number of experiments on the speed of the uniform movement during the propagation of flame in mixtures of methane (firedamp) and air through tubes of small diameter;* on the passage of flame through similar tubes filled with mixtures

* It should be remembered that the uniform movement of flame is developed only when the inflammable mixture is contained in a tube closed at one end and open at the other, ignition being effected at or near the open end.

of methane and air and open at both ends; and on the passage or projection of flame through short tubes of small diameter.

The first series of experiments—on the uniform movement of flame—serves to demonstrate the increased cooling effect of the walls of the tube as its diameter is decreased, and may be regarded as an extension of the work already referred to (*loc. cit.*, p. 1050). The main results are shown in the table on p. 659; the numbers within brackets record distances, in cm., travelled by the flames before they became extinguished; the other numbers record the speeds of the flames in cm. per second, propagation taking place throughout the lengths of the tubes; the word nil indicates that flame could not be seen to spread an appreciable distance from the secondary discharge spark used to cause ignition. Ignition was, in each instance, at a point 3 cm. from the open end of the tube; the flame was allowed to travel 30 cm. from the point of ignition and its speed over a distance of 1 metre then measured; the tubes were 3 metres in length. Each recorded result is the mean of three or four closely agreeing determinations.

There are several points of interest in this table. The apparent limits of inflammability (horizontal propagation of flame) are narrowed as the diameter of the tube is decreased until with a tube 4·5 mm. in diameter only one of the mixtures tested (containing 9·95 per cent. of methane) would propagate flame.

No attempt was made to determine for each tube the exact limiting percentages of methane required for propagation of flame, but the table should supply fairly close approximations. Thus, the tube 5·6 mm. in diameter would have as its lower limit mixture one containing less than 8·5, but more than 8·25 per cent. of methane, and as its higher limit mixture one containing more than 10·5, but less than 10·65 per cent. Bearing in mind the fact that the exact limiting mixtures were not obtained, it will be seen that the speeds of the flames tend towards a constant value of about 35 cm. per sec. as the limiting mixtures are approached. This speed can be regarded as the slowest at which continued propagation of flame in mixtures of methane and air is possible.

It follows that the higher the coefficient of conductibility of the material of which tubes of small diameter are made, the narrower are the limits of inflammability for a tube of given diameter and the larger is the diameter of tube capable of preventing the spread of flame in any mixture. Thus Davy (*loc. cit.*) found that "metallic tubes prevented explosion better than glass tubes."

In Fig. 1 a curve is given showing the relationship between the speed of the uniform movement in a 9·95 per cent. methane–air mixture and the diameter of the tube (of glass) along which the

Internal diameter of tube. Mm.	Methane in mixture. Per cent.																
	7·6	8·0	8·25	8·4	8·5	9·0	9·5	9·95	10·15	10·5	10·65	10·8	11·0	11·5	11·6	11·65	12·0
3·6	nil	nil	nil	nil	nil	nil	nil	nil*	nil	nil	nil	nil	nil	nil	nil	nil	nil
4·5	nil	nil	(20)	(18)	(20)	(20)	(20)	33·5	nil	nil	nil	nil	nil	nil	nil	nil	nil
5·6	(25)	(20)	(27)	—	36·3	38·4	40·8	41·2	40·8	38·4	nil†	nil†	nil	nil	nil	nil	nil
7·2	(37)	(30)	(30)	(30)	38·0	40·5	46·8	46·3	44·5	42·9	(60)	(53)	(43)	nil†	nil†	nil†	nil
8·1	(45)	(30).	(35)	36·5	39·3	42·4	47·7	47·4	46·7	44·0	42·2	41·0	(45)	(50)	—	—	(60)
9·0	(55)	32·6	34·8	—	40·4	44·4	48·9	48·0	47·9	46·5	45·5	—	42·5	36·9	35·5	(60)	(60)

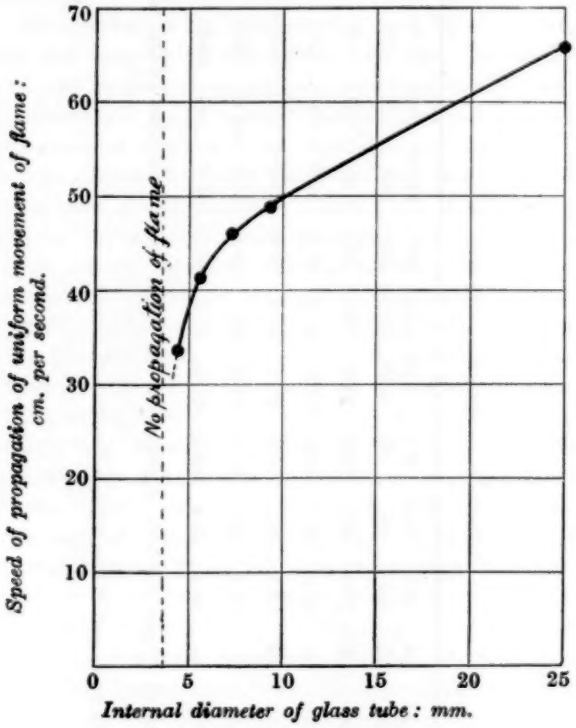
* When the flame was started in a tube 5·6 mm. in diameter and 8 cm. long it travelled 30 cm. along the 3·6 mm. tube and then died out.

† Flame travelled towards the open end of the tube, a distance of 3 cm.

flame travelled. This curve is a continuation of that shown in Fig. 4 in T., 1917, **111**, 1053, and should be compared therewith.

The Passage of Flame through Tubes Open at Both Ends.—When a mixture of methane and air contained in a horizontal tube open at both ends is ignited near one end of the tube, flame begins to travel with increasing speed towards the other end.* After a certain distance of travel, the flame vibrates backward and for-

FIG 1.



ward, and, in tubes of small diameter, becomes extinguished during any particularly rapid vibration. The distance travelled by the flame before vibrations begin depends on the length and diameter of the tube and on the percentage of methane in the mixture, being greater the longer is the tube and the larger its diameter, and less the nearer the percentage of methane approaches that required to give the fastest speed of flame (9·5 to 10 per cent. of methane in air).

* Unless the mixture is a "limit mixture," when the speed of the flame is uniform throughout its progress.

It thus results that a length of tube of diameter small enough to prevent the passage of flame in a mixture containing, say, 10 per cent. of methane in air, may fail to do so when the mixture contains only, say, 7 per cent., despite the fact that the flame in the former mixture has the greater speed. For the reason that with the 10 per cent. mixture vibrations, engendered by the rapidity with which the flame begins to move, may cause self-extinction of the flame, whilst with the 7 per cent. mixture the flame may move comparatively slowly and undisturbed throughout its course.

This fact is illustrated in the series of experiments recorded in the table that follows. The tubes were of glass and were 100 cm. long:

	Distances travelled by flame in tubes open at both ends.		
Percentage of methane in mixture	10·0	8·5	7·5
Internal diameter of tube.			
3·6 mm.	nil.	nil.	nil.
4·4 „	11·5 cm.	10 cm.	75 cm.
6·4 „	14	25 to 30	15 to 20
7·2 „	20 to 25	throughout	throughout.

Experiments of a similar nature were made with tubes of brass. The brass tubes were used as connexions between two open glass tubes 2·5 cm. in diameter and 10 cm. long, as described in the experimental portion of this paper, and their lengths were gradually shortened until flame passed from one glass tube to the other, when a mixture of methane and air was ignited near the open end of one of them. Two series of experiments were made; in one the propagation of flame was horizontal, in the other from below upwards. The results can be tabulated as shown on p. 661.

The lengths of brass tube recorded in this table represent relative distances of travel of the flames, the actual distances travelled being from 1 to 1·5 cm. less in each instance. The results for horizontal propagation of flame are shown graphically in Fig. 2, from which the greater precautions necessary to prevent the passage of flame in mixtures containing the lower percentages of methane is apparent.

The conditions under which an inflammation of firedamp takes place within a miners' safety-lamp depend on the construction of the lamp and on the manner in which it is manipulated. With some types of lamps (those receiving their air-supply from below the wick), the conditions are similar to those obtaining in the experiments just described. With others—and these constitute the majority of types—the air-supply reaches the wick from above, so that when firedamp is present in the air an inflammable mixture may occupy most of the upper portion of the lamp before it becomes

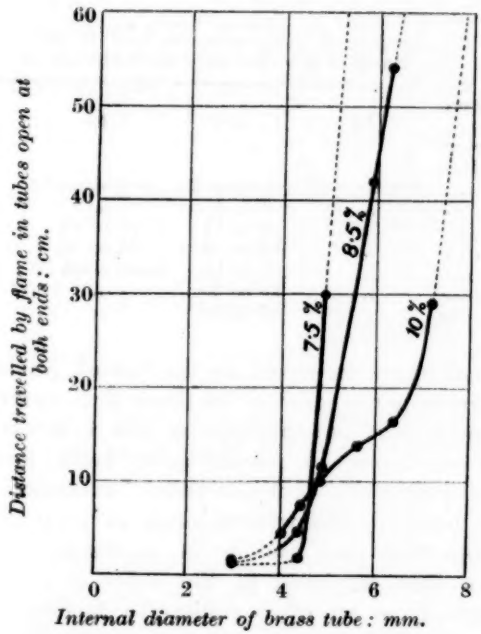
Lengths of brass tube required to prevent the passage of flame. Cm.

Percentage of methane in mixture.	10·0		8·5		7·5	
Internal diameter of tube. Mm.	Horizontal propagation.	Upward propagation.	Horizontal propagation.	Upward propagation.	Horizontal propagation.	Upward propagation.
3	less than 2	less than 2	less than 2	less than 2	less than 2	less than 2
4	4 to 5	5 to 6	2 to 3	5	less than 2	less than 2
4·4	7·5	9	4 to 5	7·5	less than 2	less than 2
4·8	10	11·5 to 12·5	11·5	18 to 19	30	30
5·6	14	15 to 16	42 to 43	50	—	—
6·4	16	18	54	55	—	—
7·2	29	32	more than 60	more than 60	—	—

ignited. Ignition is then as if near the closed end of a tube open at the other end.

Experiments were made in which a glass tube 12 cm. long and 2 cm. in diameter, closed at one end, was used as an explosion-vessel. Brass tubing of different diameters could be attached to the open end and determinations made of the lengths required to prevent the transmission of flame to an inflammable mixture of methane and air when a similar mixture was ignited by a secondary discharge 15 mm. from the closed end of the explosion-vessel, the apparatus being fixed horizontally.

FIG. 2.



With mixtures of methane and air containing either 10 or 7·5 per cent. of methane, the passage of flame from the explosion-vessel to the atmosphere outside was prevented by less than 2 cm. length of brass tubing of any diameter up to the largest tried, namely, 8 mm. In many instances, tongues of slightly luminous gases were projected from the ends of the brass tubes, but inflammation of the surrounding mixture did not follow. The question therefore arose whether increasing the speed of projection of these hot gases, by increasing the length of the explosion-vessel, would enable them to retain sufficient heat to ignite a mixture of methane

and air even after their passage through a considerable length of brass tubing of small diameter.

Experiments were therefore made in which explosion-vessels, 2 cm. in diameter, of different lengths were employed, so that the flames in 10 per cent. mixtures of methane and air, ignited at the closed ends of the explosion-vessels, would acquire different speeds by the time they reached the open ends. Previous experiments had shown that the speed of flame in a 10 per cent. mixture of methane and air contained in a horizontal glass tube 2 cm. in diameter, closed at one end and open at the other, increases progressively with its distance of travel from the closed end over distances of 3 or 4 metres. The results were as follow:

Length of explosion-vessel. Cm. ..... / Internal diameter of brass tube. Mm.	Length of brass tube required to prevent passage of flame in a 10 per cent. methane–air mixture. Cm.			
	12	20	30	40
4	less than 2	less than 2	less than 2	3 to 4
4·4	„	3 to 4	„	3 to 4
4·8	„	13 to 14	16 to 18	more than 30
5·6	„	16 to 18	24 to 25	„
6·4	„	18 to 19	more than 30	„
7·2	„	19 to 20	„	„
8·0	„	19 to 20	„	„

The increased speed imparted to the heated products of combustion by increasing the speed of the flame thus materially reduces the protection against inflammation of the external atmosphere afforded by brass tubes. A miners' safety-lamp, however, rarely has an effective length of "explosion-vessel" exceeding 12 to 15 cm. On the other hand, its diameter is often as great as 6 cm. It seemed possible that the use of an explosion-vessel of larger diameter than that employed in the series of experiments just described might have an effect similar to increasing its length, inasmuch as the higher pressures produced within a vessel of greater capacity would project the heated products of combustion through the brass tubes with greater speed.

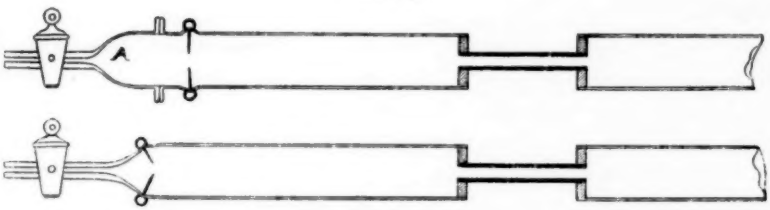
On trial, however, this was found not to be so. An explosion-vessel 7·5 cm. in diameter and 12 cm. long was no more effective in transmitting inflammation through brass tubes to the external atmosphere than one 2 cm. in diameter. Furthermore, when the length of this larger explosion-vessel was increased to 40 cm., it was found that protection was still afforded by a length of brass tube of less than 2 cm. of any diameter up to 8 mm., the largest tried. Increasing the capacity of the explosion-vessel thus actually

decreased the danger of the inflammation being conveyed to the external atmosphere.

These results, which were repeated many times with mixtures of different methane-content, are in conformity with some remarkable experiments by Beyling ("Verein für die Bergbaulichen Interessen im oberbergamtbezirk Dortmund." Essen, 1906), made primarily to determine the best means of rendering electrical machinery flame-proof. Beyling used an explosion-vessel 33·5 cm. in diameter and 42·5 cm. long (capacity, 42 litres), and found that when a mixture of firedamp and air containing 9 per cent. of methane was ignited at one end of the vessel, a hole more than 4 cm. in diameter could exist at the other end without danger of a similar mixture outside being ignited.

The explanation of these results is that the products of combustion, being under a fairly high pressure within the explosion-vessels of large capacity, were rapidly expanded as they issued

FIG. 3.



through the holes or tubes, and were thus cooled below the temperature at which they could ignite the mixture outside.

EXPERIMENTAL.

The experimental work can be divided into two portions, that dealing with the speed of flame in tubes of small diameter, and that relating to the passage of flame through short lengths of such tubes from vessels filled with inflammable mixtures.

The motion of the most rapid flame studied was sufficiently slow to follow by eye, so that for the measurements of speeds it sufficed to record the times at which the flames made their appearance at fixed points along the tubes. This was done by the use of a tapping-key in electrical connexion with a chronograph.

The different forms of apparatus used in the experiments on the passage of flame through short lengths of tubes are shown in Fig. 3. The upper diagram illustrates the means employed to study the passage of flame through tubes open at both ends. The ground-

glass cover, *A*, was removed just before igniting the mixture by sliding it downwards, so as to avoid disturbance of the mixture within the tube. The whole apparatus, including the glass extension beyond the length of brass tube undergoing test, was filled with the requisite mixture by displacement of air, six times the volume of the apparatus being taken for displacement.

The lower diagram shows the arrangement when testing the conditions necessary for the passage of flame from a closed vessel, and is self-explanatory.

The methane used throughout the experiments was from firedamp obtained from a blower in South Wales; it contained 2 per cent. of nitrogen as its only impurity. The mixtures were stored over water in metal or glass gas-holders of suitable capacity, and were analysed before use.

These experiments have been carried out for the Mines Department of the Home Office. They complete part of a research on miners' safety-lamps which will form the subject of an official report.

[*Received, July 12th,* 1918.]

LVII.—*The Relative Activities of Methyl, Ethyl, and* n-*Propyl Iodides with Sodium α- and β-Naphthoxides.*

By Henry Edward Cox.

The reactivity of the alkyl iodides with a variety of compounds has been measured by many investigators.

It has usually been found that methyl iodide is many times more active than ethyl iodide, and ethyl iodide is from one to five times as active as *n*-propyl iodide; several anomalies have been recorded, however, including one instance in which ethyl iodide is twice as reactive as methyl iodide. It seemed of interest to examine the relative activities of these substances with further bases, and as the naphthoxides are very similar in chemical behaviour, it was decided to examine whether there is any difference in their reactivities with the alkyl haloids; methyl, ethyl, and *n*-propyl iodides were chosen, as it has been found in all recorded work that the higher members of the series show a perfectly regular and gradual diminution in activity with increasing molecular

weight, whereas the first three members have shown considerable divergence.

The following table shows the results on record for these iodides calculated in terms of *n*-propyl iodide=1:

	Methyl.	Ethyl.	*n*-Propyl.
Triethylamine in acetone[1]	590·7	5·24	1·00
Sodium ethoxide in ethyl alcohol[2]	36·13	2·85	1·00
Potassium ethoxide ,, ,, ,, [2]	35·53	2·78	1·00
Sodium methoxide ,, ,, ,, [2]	16·31	2·51	1·00
Potassium methoxide ,, ,, [2]	16·41	2·45	1·00
Dimethylaniline ,, ,, ,, [3]	48·00	3·2	1·00
Tri*iso*amylamine ,, ,, ,, [3]	327·0	4·2	1·00
Sodium ethyl acetoacetate ,, [4]	39·2	4·2	1·00
Silver nitrate ,, ,, ,, [5]	0·94	2·2	1·00
Sodium phenoxide ,, ,, ,, [6]	12·1	2·5	1·00

[1] Menschutkin, *Zeitsch. physikal. Chem.*, 1890, **5**, 589.
[2] Hecht, Conrad, and Bruckner, *ibid.*, 1889, **4**, 273, 649.
[3] Preston and Jones, T., 1912, **101**, 1930.
[4] Wislicenus, *Annalen*, 1882, **212**, 239.
[5] Burke and Donnan, T., 1904, **85**, 555.
[6] Segaller, T., 1913, **103**, 1154.

There are also many figures on record for methyl and ethyl iodides only. In the above table, there is a very marked increase in activity of methyl iodide with triethylamine and with tri*iso*amylamine, which contrasts very strongly with the fact that ethyl iodide is twice as reactive as methyl iodide with silver nitrate.

It is well known that the naphthols are esterified more readily than the phenols, so that it might be anticipated that the velocity constants would be higher than with phenoxides and lower than with ethoxides. This expectation is borne out by the results obtained.

Sodium α-naphthoxide is slightly more reactive than the β-compound, and it was found that the difference is slightly accentuated as the molecular weight of the alkyl group increases; thus at concentration $N/5$, the ratio k_α/k_β is:

Methyl iodide.....	1·12
Ethyl iodide	1·23
n-Propyl iodide	1·32

This greater activity of the α-compound with *n*-propyl iodide makes the relative activity of the iodides rather less with the α- than with the β-naphthoxide. At the same concentration, $N/5$, was found:

	α-Naphthoxide.	β-Naphthoxide.
Methyl iodide	7·41	8·82
Ethyl iodide	1·99	2·16
n-Propyl iodide	1·00	1·00

These results all refer to the reaction in ethyl alcohol at 40°. The reaction is bimolecular, as is to be expected from the equation.

There is, however, a possibility of a side-reaction taking place, such as the formation of olefines or ethers. This is suggested by the fact that the velocity constant decreases slightly as the reaction proceeds; this decrease has been observed by nearly all workers with alkyl iodides. It does not seem probable that it is due to loss of alkyl iodide, as it is observed even at low temperatures and when working in sealed tubes. It is also observed in the presence of an excess of alkyl iodide. The decrease is not due to neutral-salt action, as it is found that addition of sodium iodide has no appreciable effect on the velocity constant.

It was also observed that, particularly in the more concentrated solutions, the reaction mixture, which is practically colourless at the start, darkens as the reaction proceeds. This takes place even though the flask is not opened or exposed to the air. The colour is not due to the liberation of iodine.

The question also arises whether the equation,

$$C_2H_5\cdot ONa + C_{10}H_7\cdot OH \longrightarrow C_2H_5\cdot OH + C_{10}H_7\cdot ONa$$

is reversible or not. If alcoholysis takes place, sodium ethoxide will be formed; the velocity coefficients for sodium ethoxide and the alkyl iodides are several times larger than those of the naphthoxides with the corresponding iodides. The velocity constant would therefore show a markedly higher value at the commencement of an experiment, and would rapidly fall off as the ethoxide disappears, and the increasing concentration of free naphthol retards the further alcoholysis of the naphthoxide. A rapid decrease in the value of the constant would be found if there is much alcoholysis.

In the experiments here described, there is a gradual diminution in the value of the constant, but it is not large; indeed, in most experiments it is not larger than the decrease observed by Hecht and Conrad in their work on the ethoxides, where the case of alcoholysis does not arise. In order to obtain some information on this point, experiments were made in $N/10$-solution with methyl iodide and sodium α- and β-naphthoxides containing 5 per cent. excess of the corresponding naphthol; this would suppress alcoholysis, and consequently decrease the constant. The effect observed was that the constant is decreased by 7·3 per cent. in the case of the α-naphthoxide and by 10·7 per cent. in the case of the β-naphthoxide, but there was still observed the gradual decrease in the value of k.

The effect of the increased viscosity by the excess of naphthol

would no doubt slightly decrease the constant, but not to so great an extent. It is interesting to note that Robertson and Acree (*Amer. Chem. J.*, 1913, **49**, 474) found that a decrease of 7 per cent. was produced by 5 per cent. excess of phenol in the reaction between sodium phenoxide and methyl iodide at concentration $N/2$.

Effect of Initial Concentration on the Velocity Coefficients.

This point is one of considerable importance. Hecht, Conrad, and Brückner (*Zeitsch. physikal. Chem.*, 1890, **5**, 289) proposed the formula $k_v = k_1 + a \log v$, where v is the volume in litres which would contain one gram-molecular weight of the reacting substances.

This empirical equation has been found to hold remarkably well in several reactions of the kind here considered. Schröder and Acree (T., 1914, **105**, 2582) have given a scientific basis to this equation, which greatly enhances its interest. They show also that at a given dilution corresponding with complete ionisation of one of the reacting substances, the equation would no longer hold.

The effect of initial concentration has been tried by measuring the velocity of the reaction in equivalent concentrations from $N/1$ to $N/40$. The velocity coefficient increases with dilution in each case, and it increases more rapidly in the case of the α-naphthoxide than with the β-naphthoxide.

The increase is large with methyl iodide, less with ethyl and still less with *n*-propyl iodide; this is quite in accord with the results of Hecht, Conrad, and Brückner. The equation $k_v = k_1 + a \log v$ is found to hold for ethyl and propyl iodides at least up to dilution $v = 40$. With methyl iodide and the α- and β-naphthoxides, the equation holds from $v = 1$ up to $v = 10$ and $v = 7$ respectively; thereafter the value of k_v increases abnormally rapidly. Figs. 1 and 2, obtained by plotting actual values of k against $\log v$, show the increase with dilution. Each point lying off the straight line has been determined in duplicate.

It is most unlikely that ionisation of the naphthoxides would be complete at as low a dilution as $N/10$, so that Schröder and Acree's prediction cannot be applied.

Also, if the increase is due to alcoholysis or ionisation, or to any change in the naphthoxide, it would be expected that a similar rise would be observed with ethyl and propyl iodides at perhaps slightly greater dilution.

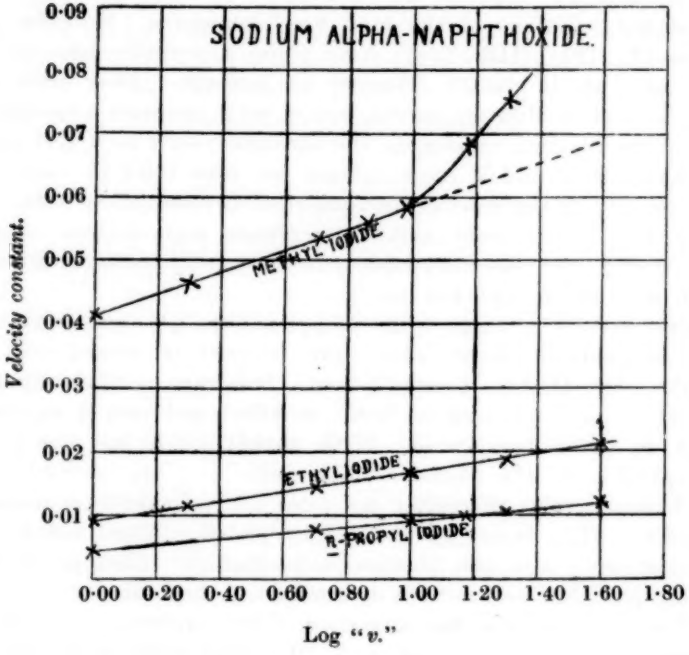
Up to $v = 40$, no such rise is observed, so that it appears probable that this abnormality is due to some specific effect with methyl iodide only.

Experimental.

All the reactions were carried out with ethyl alcohol as solvent; the alcohol was prepared by digesting commercial absolute alcohol with calcium oxide and calcium for several hours, and then redistilling from calcium.

The naphthoxides were prepared from the purest obtainable α- and β-naphthols, quite white, melting at 94° and 122° respectively. The calculated quantity of sodium dissolved in ethyl alcohol was added to an alcoholic solution of the naphthol, and the

Fig 1.



solution evaporated to dryness in a vacuum at 100°. The products were almost white. (Found: Na = 13·75 and 13·87 respectively. Calc.: Na = 13·86 per cent.)

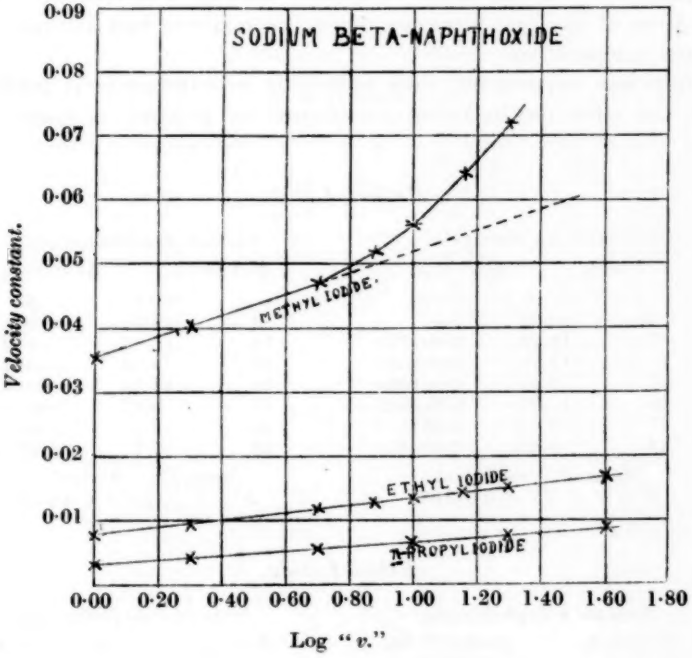
Some of the duplicate experiments were made by mixing solutions of sodium ethoxide and naphthol in the proper proportions just before use. This method gave results identical with those obtained by weighing out the dry compound, and has been applied

successfully by Hecht and Conrad and by Robertson and Acree in their work on phenoxides. It is very convenient in the case of the α-naphthoxide, as this salt is very sensitive to air and moisture and rapidly turns brown on exposure.

Tymstra and Eggink's method (*Ber.*, 1906, **39**, 14) was tried, but without success, minute balls of sodium being retained even after prolonged heating.

Methyl and ethyl iodides were purified by washing with dilute alkali, then with water, drying over fused calcium chloride, and

FIG. 2.



redistilling from ignited silver. The boiling points were 42·5—43° and 71·5—72° respectively. *n*-Propyl iodide was obtained from propyl alcohol by Bancel's method (*Bull. Soc. chim.*, 1883, [ii], **39**, 648) and purified as above. It boiled at 101—101·5°.

The temperature was maintained at 40·0° by means of a thermostat fitted with an Ostwald toluene regulator and an efficient stirring gear.

The requisite quantities of reagents were weighed out, dissolved separately, and the solutions mixed. After allowing time for the

mixture to attain the temperature of the bath, 5 c.c. were withdrawn by a pipette, kept at 40°, calibrated to deliver a volume equal to 5 c.c. at 15°.

This was run into cold water containing almost enough standard hydrochloric acid to neutralise the unchanged naphthoxide, and the titration completed as rapidly as possible, using lacmoid as indicator.

The results were calculated from the equation $k' = \frac{1}{t} \cdot \frac{x}{a \cdot (a-x)}$, in terms of c.c. of acid used for titration, then brought to k in terms of gram-molecules per litre by multiplying by five times the dilution "v" of the acid. Time in minutes was reckoned from the time of the first titration when the mixture had attained the proper temperature.

Only one experiment with each pair of substances is given in full, the other results being summarised for economy of space.

Methyl Iodide.

Sodium α-naphthoxide.

$N/1$ each. Acid $N/5$.

t.	$a-x$.	k'.
0	23·35	—
7	18·25	0·001719
15	14·70	0·001680
22	12·65	0·001646
30	11·00	0·001603
37	9·75	0·001614
44	8·85	0·001595

Mean $k' = 0·001643$.
$k = k' \times 25 = 0·04108$.

Sodium β-naphthoxide.

$N/1$ each. Acid $N/5$.

t.	$a-x$.	k'.
0	21·70	—
14	15·05	0·001454
21	13·05	0·001455
30	11·15	0·001454
41	9·65	0·001404
50	8·65	0·001390
60	7·75	0·001382

Mean $k' = 0·001423$.
$k = k' \times 25 = 0·03558$.

Ethyl Iodide.

Sodium α-naphthoxide.

$N/5$ each. Acid $= N/10$.

t.	$a-x$.	$k' \times 10^3$.
0	9·85	
60	8·43	0·2850
130	7·18	0·2905
234	5·95	0·2845
290	5·43	0·2850
350	5·00	0·2813
410	4·65	0·2769

Mean $k' = 0·0002839$.
$k = k' \times 50 = 0·01420$.

Sodium β-naphthoxide.

$N/5$ each. Acid $= N/10$.

t.	$a-x$.	$k' \times 10^3$.
0	9·70	—
85	8·08	0·2376
160	7·10	0·2359
235	6·33	0·2335
300	5·78	0·2330
360	5·43	0·2251
420	5·05	0·2260

Mean $k' = 0·0002318$.
$k = k' \times 50$ 0·01159.

n-*Propyl Iodide.*

Sodium α-naphthoxide.

$N/10$ each. Acid $= N/20$.

t.	$a-x$.	$k' \times 10^4$.
0	9·55	—
140	8·55	0·8748
247	7·90	0·8856
384	7·30	0·8406
540	6·65	0·8456
586	6·48	0·8464
630	6·35	0·8376

Mean $k' = 0{\cdot}00008551$.
$k = k' \times 100 = 0{\cdot}008551$.

Sodium β-naphthoxide.

$N/10$ each. Acid $= N/20$.

t.	$a-x$.	$k' \times 10^4$.
0	9·65	—
140	8·85	0·6693
247	8·35	0·6532
384	7·80	0·6402
540	7·25	0·6353
587	7·02	0·6616
630	6·90	0·6555

Mean $k' = 0{\cdot}00006525$.
$k = k' \times 100 = 0{\cdot}006525$.

Summary of Results.

Methyl Iodide.

Sodium α-naphthoxide.

v.	k_v (found).	k_v (calc.).
1	0·04108	0·04108
2	0·04693	0·04623
5	0·05307	0·05303
7·5	0·05555	0·05604
10	0·05864	0·05818
15	0·06844	—
20	0·07513	—

"a" = 0·0171.

Sodium β-naphthoxide.

k_v (found).	k_v (calc.).
0·03556	0·03556
0·04060	0·04059
0·04725	0·04723
0·05235	0·05019
0·05590	—
0·06487	—
0·07209	—

"a" = 0·0167.

Ethyl Iodide.

Sodium α-napthoxide.

v.	k_v (found).	k_v (calc.).
1	0·009185	0·009185
2	0·01166	0·01135
5	0·01422	0·01422
7	—	—
10	0·01636	0·01638
15	—	—
20	0·01860	0·01855
40	0·02109	0·02072

"a" = 0·00720.

Sodium β-naphthoxide.

k_v (found).	k_v (calc.).
0·007900	0·007900
0·009908	0·009646
0·01159	0·01195
0·01250	0·01280
0·01402	0·01370
0·01453	0·01472
0·01568	0·01545
0·01700	0·01719

"a" = 0·00580.

n-*Propyl Iodide.*

Sodium α-naphthoxide.

v.	k_v (found).	k_v (calc.).
1	0·004300	0·004300
5	0·007133	0·007355
10	0·008551	0·008670
20	0·01011	0·009985
40	0·01121	0·001130

"a" = 0·00437.

Sodium β-naphthoxide.

k_v (found).	k_v (calc.).
0·003160	0·003160
0·005355	0·005431
0·006525	0·006410
0·007392	0·007388
0·008517	0·008367

"a" = 0·00325.

Sodium α-naphthoxide containing 5·0 per cent. excess of α-naphthol with methyl iodide, $N/10$ each.

$k = 0{\cdot}05436$; decrease in $k = 7{\cdot}30$ per cent.

Sodium β-naphthoxide containing 5·0 per cent. excess of β-naphthol with methyl iodide, $N/10$ each.

$k = 0{\cdot}04989$; decrease in $k = 10{\cdot}75$ per cent.

Conclusions.

The reaction of the alkyl iodides with sodium α-naphthoxide and sodium β-naphthoxide is a bimolecular one of a special type, in which the velocity of reaction is dependent on the initial concentration.

There is some evidence that both naphthoxides undergo alcoholysis in ethyl-alcoholic solution.

Sodium α-naphthoxide is more reactive towards the alkyl iodides than is sodium β-naphthoxide.

The presence of an excess of α- or β-naphthol decreases the velocity coefficient.

The velocity of the reaction in each case increases with dilution. The increase is most marked with methyl iodide, and becomes less as the molecular weight of the alkyl group increases.

The velocity of reaction at dilution "v" can be expressed in the form of an equation $k_v = k_1 + a \log v$. This equation holds good with ethyl and *n*-propyl iodides at least so far as dilution $v = 40$. With methyl iodide, the equation holds only up to dilution $v = 10$ for sodium α-naphthoxide and $v = 7$ for the β-compound; at higher dilution, methyl iodide exhibits abnormal reactivity.

The order of relative activity is methyl, ethyl, *n*-propyl. Methyl iodide is several times more active than ethyl iodide at the same dilution; this is in agreement with the majority of the published results for these iodides.

The author wishes to express his thanks to Mr. G. R. Thompson, who has provided every facility for this work; also to Dr. J. C. Crocker for his kind interest and valuable advice.

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LVIII.—*The Ternary System—Sodium Sulphate, Ammonium Sulphate, and Water. The Utilisation of Nitre Cake for the Production of Ammonium Sulphate.*

By Harry Medforth Dawson.

In connexion with experiments instituted with the object of finding a method for the separation of sodium sulphate and ammonium sulphate from solutions containing both these substances, and with a view to the possible use of solutions of nitre cake for the absorption of ammonia in the manufacture of ammonium sulphate, an investigation has been made of the equilibrium relations in the system Na_2SO_4–$(NH_4)_2SO_4$–H_2O. This investigation was completed during 1917, and although it was originally intended to defer the publication of the results for the present, the appearance of a series of papers by Matignon and Meyer (*Compt. rend.*, 1917, **165**, 787; 1918, **166**, 115, 686) on the equilibrium conditions in this system has led the author to revise his original proposal.

The components of this system combine to form two compounds, namely, Glauber's salt and the double salt $Na_2SO_4,(NH_4)_2SO_4,4H_2O$, and the characteristic features of the system are largely determined by the properties of these compounds. The double salt seems to have been first obtained by Séguin (*Ann. Chim. Phys.*, 1814, **91**, 219), and subsequently its formation by the interaction of ammonium chloride and Glauber's salt and by the action of water on a mixture of sodium chloride and ammonium sulphate was described by Schiff (*Annalen*, 1860, **114**, 68). The crystallographic properties of the double sulphate have been examined on several occasions by Mitscherlich (*Ann. Phys. Chem.*, 1843, [ii], **58**, 469), Lang (*Wien Akad. Ber.*, 1862, **45**, 108), Reinsch (*Zeitsch. Kryst. Min.*, 1884, **9**, 561), and Retgers (*Zeitsch. physikal. Chem.*, 1891, **8**, 58), but the conditions of formation of the double salt and its relation to the simple salts do not appear to have been previously examined. According to Retgers (*loc. cit.*), crystals of the anhydrous double sulphate separate out at temperatures between 50° and 70°, but the crystals actually obtained by this observer were very small and impure, and the view that they represent the anhydrous double sulphate was based on the optical behaviour of the crystals when examined under the microscope.

In preliminary experiments, it was found that finely powdered Glauber's salt and ammonium sulphate react together at the

ordinary temperature, the mixture becoming pasty and the temperature falling considerably. Although it was at first suspected that this might be due to the simple dehydration of the Glauber's salt in the presence of ammonium sulphate, further experiments showed that the reaction consists in the formation of the double salt in accordance with the equation

$$Na_2SO_4,10H_2O + (NH_4)_2SO_4 = Na_2SO_4,(NH_4)_2SO_4,4H_2O + 6H_2O.$$

If the finely powdered substances are mixed together whilst the temperature is kept at $-15°$ to $-20°$, there is no evidence of the above reaction, the mixture remaining perfectly dry, but at $-10°$, on the other hand, the mixture shows distinct signs of caking, and it thus seemed probable that the above reaction sets in at some temperature between $-10°$ and $-20°$.

Lowering of the Temperature of Transition of Glauber's Salt on the Addition of Ammonium Sulphate.—In experiments made to determine the effect of ammonium sulphate on the temperature at which Glauber's salt is transformed into anhydrous sodium sulphate, about 100 grams of Glauber's salt were heated to about 40° and cooling curves taken before and after the addition of measured quantities of ammonium sulphate. During the cooling, the tube containing the mixture was surrounded by cotton-wool and the mixture thoroughly stirred. The results obtained are shown in table I.

TABLE I.

Reference number.	Nature of cooling system.					Transition temperature.
a	Glauber's salt.					32·35°
b	100 grams	Glauber's salt	+4·66 grams		$(NH_4)_2SO_4$	30·05
c	,,	,,	+9·33	,,	,,	27·75
d	,,	,,	+18·65	,,	,,	26·50
e	,,	,,	+26·60	,,	,,	26·50
f	,,	,,	+43·8	,,	,,	continuous fall in temperature.

The value of the molecular lowering of the transition temperature calculated from observations *b* and *c* is 65, which is slightly less than the value obtained by Loewenherz (*Zeitsch. physikal. Chem.*, 1895, **18**, 70) for relatively dilute solutions of the alkali sulphates. The limiting temperature, 26·5°, obviously represents an invariant point, and, in point of fact, the three solid phases in equilibrium with the solution are Glauber's salt, anhydrous sodium sulphate, and the double salt $Na_2SO_4,(NH_4)_2SO_4,4H_2O$.

Decomposition of the Double Salt.—In view of Retgers's observation that the crystals deposited at higher temperatures are anhydrous, it was to be expected that the double salt would decom-

pose at some temperature below 70°. Preliminary experiments, in which a dilatometer was filled with the finely powdered double salt, gave no positive evidence of this change. On the other hand, when a mixture of 50 grams of Glauber's salt and 30 grams of ammonium sulphate was heated to about 80° and allowed to cool in the air, the temperature remained stationary at 58—59°. In a further experiment, in which the tube containing the mixture was jacketed and allowed to cool with the outside tube immersed in a water-bath at 50°, the temperature of the mixture fell slowly to 58·2° and then rose to 59·3°, at which it remained constant for a very considerable time. This temperature was evidently to be regarded as that corresponding with a further invariant point, and it seemed probable that this was the temperature of decomposition of the hydrated double salt.

Solubility Measurements.—Further information was sought by solubility measurements, the chief object of which was to ascertain the composition of the solutions which are characteristic of the invariant and univariant systems. In the case of the invariant systems, the solutions in question are saturated with respect to three solid phases, and the temperature has a definite value. On the other hand, the temperature is variable in the case of the univariant systems which are characterised by the presence of two solid phases, but at a given temperature the concentration of both the sodium sulphate and the ammonium sulphate has a definite value.

In connexion with the solubility measurements, a quantity of the double salt was prepared by dissolving sodium sulphate and ammonium sulphate in the molecular proportion 1:2 to give a solution of the approximate molecular composition

$$1000H_2O : 40Na_2SO_4 : 80(NH_4)_2SO_4.$$

The warm solution was allowed to cool to the ordinary temperature, and crystals of the double salt were deposited, which, after drying in contact with the air, gave on analysis $Na_2SO_4 = 40·7$ (theory, 41·0 per cent.) and $(NH_4)_2SO_4 = 38·3$ (theory, 38·15 per cent.).

Preliminary measurements of the quantities of sodium and ammonium sulphates in the solutions saturated at 0°, 25°, 50°, and 100° were made in order to ensure the presence of the requisite solid phases in the subsequent experiments. In making the final determinations, a solution having approximately the composition of the saturated solution was prepared, and when the temperature of this had been brought to the desired value, the requisite solid phases in finely powdered form were added in considerable quantity. The mixture was stirred for one to two hours, and a sample of the saturated solution, filtered through a cotton-wool plug, was removed

for analysis. The sodium sulphate was estimated by evaporation of a measured fraction to dryness in a platinum dish, and subsequently heating the residue to redness. It was found advisable to treat the residue with a little ammonia, and to repeat these operations before the sodium sulphate was finally weighed. For the estimation of the ammonium sulphate, a second fraction was added to an excess of standard sodium hydroxide, and, after boiling, the excess of alkali was titrated by means of standard acid.

The results obtained in the solubility experiments are shown in table II, in which are recorded the temperature, the nature of the solid phases in contact with the solution, and also the weight and molecular composition of the solution.

The relations exhibited by the solubility data recorded in the table on p. 679 are shown in Fig. 1, in which temperature is given by the abscissa, whilst the ordinate represents the number of molecules of sodium sulphate *or* ammonium sulphate per 1000 molecules of water. Two groups of curves are thus obtained, the lower one of which has reference to the sodium sulphate content of the saturated solutions and the higher one to the amount of ammonium sulphate. Corresponding points in the two groups are indicated by the same letters, the ammonium sulphate group being distinguished by a dash. The points D and D' thus represent the numbers of molecules of sodium sulphate and ammonium sulphate respectively per 1000 molecules of water in the solution which is characteristic of the invariant system at the temperature of decomposition of the double salt into the component simple sulphates. In exactly the same way, the curves which connect such corresponding points are corresponding curves. The curves which represent solutions saturated with respect to Glauber's salt and ammonium sulphate (AB and $A'B'$), with respect to double salt and ammonium sulphate (BD and $B'D'$), and with respect to anhydrous sodium sulphate and ammonium sulphate (DE and $D'E'$), do not exhibit any peculiarity which calls for special comment. The case is different, however, when we consider the curves which correspond with solutions saturated with respect to double salt and Glauber's salt, and those which represent solutions saturated with respect to double salt and anhydrous sodium sulphate. The curves BC and $B'C'$ show that in solutions saturated in regard to double salt and Glauber's salt, the sodium sulphate content increases rapidly with rise of temperature, whilst the ammonium sulphate concentration rapidly decreases. Between $-16°$, which, according to the curves in Fig. 1, appears to be the temperature of formation of the double salt, and $26{\cdot}5°$, at which Glauber's salt is transformed into the anhydrous sulphate, the

TABLE II.

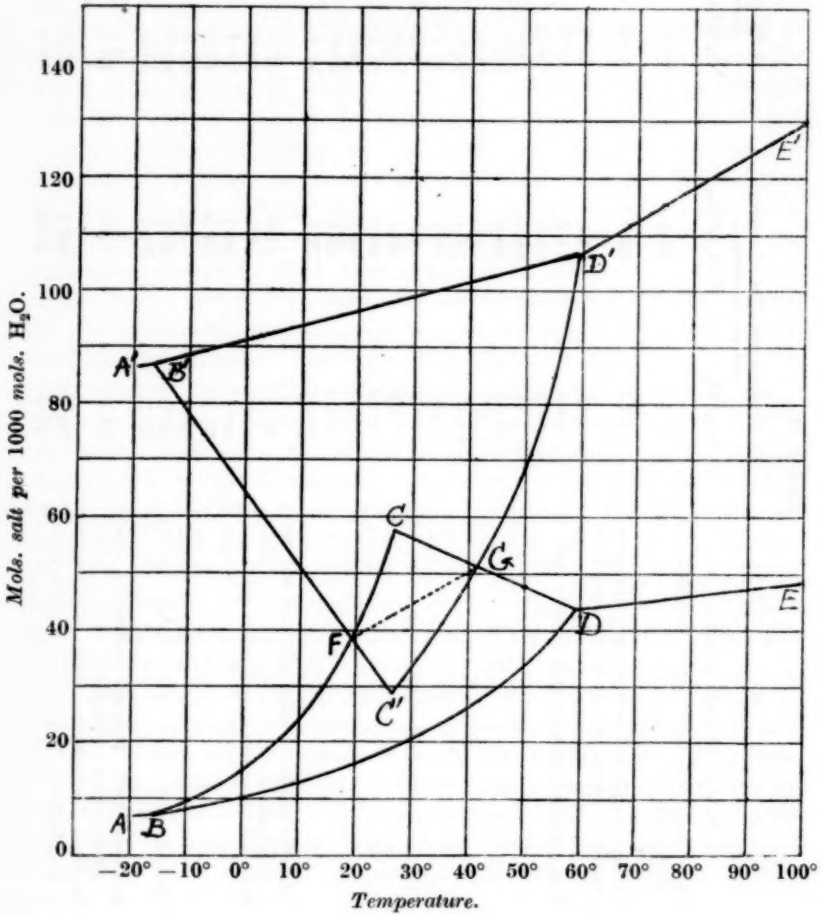
Temperature.	Nature of solid phases.	Grams per 100 of water		Mols. per 1000 of water.	
		Na_2SO_4.	$(NH_4)_2SO_4$.	Na_2SO_4.	$(NH_4)_2SO_4$.
−19·5° (cryohydric temperature).	Ice, Glauber's salt, and ammonium sulphate	5·29	63·5	6·70	86·6
−18·0°	Glauber's salt and ammonium sulphate.	5·40	63·5	6·85	86·6
−16·0	Glauber's salt, ammonium sulphate, and double salt	5·32	63·6	6·75	86·8
−13·0	Ammonium sulphate and double salt	5·68	64·9	7·20	88·5
−10·0	,, ,,	6·33	65·6	8·03	89·2
0·0	,, ,,	7·81	66·7	9·9	91·0
15·0	,, ,,	10·85	69·6	13·75	94·9
25·0	,, ,,	14·6	71·0	18·5	96·8
40·0	,, ,,	19·7	75·1	25·0	102·4
50·0	,, ,,	25·8	76·1	32·7	103·8
−13·0	Glauber's salt and double salt	6·52	58·6	8·26	79·9
−10·0	,, ,,	7·78	56·1	9·86	76·5
0·0	,, ,,	12·05	46·6	15·25	63·5
15·0	,, ,,	22·9	33·3	29·0	45·4
20·0	,, ,,	31·5	28·9	39·9	39·4
25·0	,, ,,	40·9	22·1	51·8	30·2
26·5	Glauber's salt, double salt, and sodium sulphate	45·2	21·0	57·3	28·6
35·0	Sodium sulphate and double salt	41·7	28·7	52·9	39·2
40·0	,, ,,	40·5	34·7	51·3	47·3
50·0	,, ,,	37·2	50·5	47·2	68·9
55·0	,, ,,	36·0	62·0	45·6	84·6
25·0	Double salt	32·9	30·5	41·6	41·6
35·0	,,	37·3	34·7	47·3	47·3
59·3	Double salt, sodium sulphate, and ammonium sulphate	34·3	77·7	43·5	106·0
75	Sodium sulphate and ammonium sulphate	36·1	84·3	45·7	115·0
100	,, ,,	37·9	95·0	48·0	129·5

molecular ratio of ammonium sulphate to sodium sulphate in the saturated solution falls from about 12·8 to 0·50.

The curves CD and $C'D'$, which represent solutions saturated with respect to double salt and anhydrous sodium sulphate, follow an opposite course, in that the sodium sulphate content decreases

FIG. 1.

Na_2SO_4—$(NH_4)_2SO_4$—H_2O.



with rise of temperature, whilst the ammonium sulphate concentration increases rapidly. Between 26·5° and 59·3°, at which the double salt is decomposed, the molecular ratio of ammonium sulphate to sodium sulphate increases from 0·50 to 2·44.

The point F, at which the curves BC and $B'C'$ intersect, and

the point G, corresponding with the intersection of CD and $C'D'$, represent respectively the lower and upper limits of the temperature interval within which the double salt is not decomposed in contact with water. The limiting temperatures are approximately 20° and 41·5° respectively, and it is only within this range that solutions saturated with respect to double salt and sodium sulphate (Glauber's salt below 26·5° and anhydrous sodium sulphate above 26·5°) contain a larger molecular quantity of sodium sulphate than of ammonium sulphate. Below 20°, the double salt is decomposed by water with the separation of Glauber's salt, and above 41·5° it is similarly decomposed with the separation of anhydrous sodium sulphate. The dotted curve joining the points F and G represents the curve of solubility of the double salt. In practice, it is possible to measure the solubility of the double salt at temperatures outside the interval corresponding with FG, but the saturated solutions so obtained are meta-stable.

The graph of the solubility data in Fig. 1 shows clearly that the two ammonium sulphate curves, as well as the two sodium sulphate curves, intersect at about −16°, and it is probable that this represents the temperature at which the double salt is formed from Glauber's salt and ammonium sulphate. Further evidence in support of the existence of this lower limiting temperature is afforded by observations on the cooling of certain mixtures of the components. Suitable mixtures are obtained by mixing finely powdered Glauber's salt and ammonium sulphate in the molecular proportion 2:3, with the addition of a little water to reduce the stiffness of the pasty mass which is formed by their interaction. The tube containing this mixture was fitted with a thermometer and stirrer, and surrounded by a wider glass tube immersed in a freezing mixture at −22°. The following readings were taken after successive five-minute intervals: −11·0°, −13·1°, −14·5°, −15·5°, −16·5°, −17·0°, −17·5°, −18·0°, −18·2°, −18·5°, −18·3°, −18·0°, −17·9°, −17·2°, −16·9°, −16·6°, −16·3°, −16·0°, −16·1°, −16·3°, −16·5°. According to this record, the temperature fell to −18·5° and then rose to −16·0°, which represents the temperature of formation of the double salt, and agrees closely with the temperature indicated by the solubility curves.

Crystallisation of Solutions containing Sodium and Ammonium Sulphates.—According to the graph of the solubility data in Fig. 1, it is evident that the crystallisation of a solution, which contains equimolecular quantities of the two sulphates, will yield the pure double salt if the temperature of the solution lies between 20° and 41·5°.

In an actual experiment, in which a solution, prepared by dis-

solving 284 grams of sodium sulphate and 264 grams of ammonium sulphate in 720 grams of water, was allowed to cool to 20°, 180 grams of the double salt were obtained. This result corresponds closely with that calculated from the equation:

$$1000H_2O : 50Na_2SO_4 : 50(NH_4)_2SO_4 = 13{\cdot}0Na_2SO_4,(NH_4)_2SO_4,4H_2O + 0{\cdot}948[1000H_2O : 39Na_2SO_4 : 39(NH_4)_2SO_4].$$

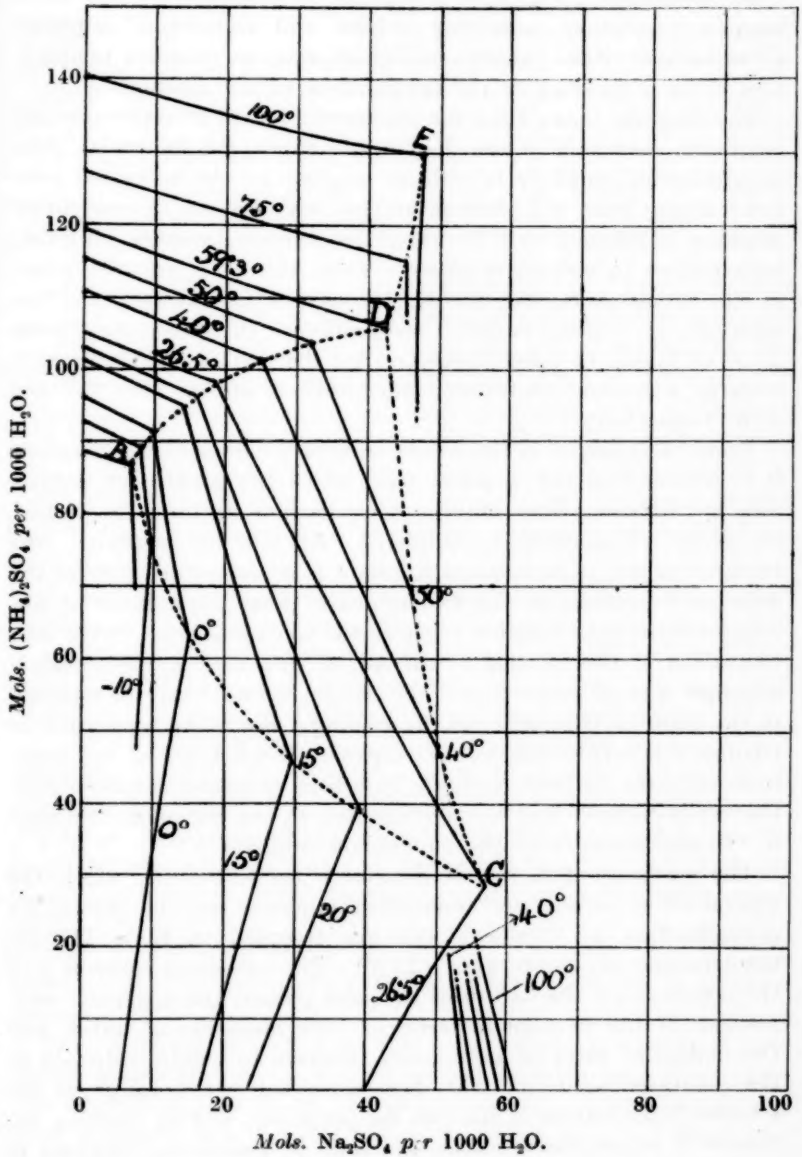
With regard to the separation of sodium and ammonium sulphates by crystallisation from a solution containing the mixed sulphates, it should be noted that there is a great disparity at low temperatures in the quantities of the two sulphates which are contained in solutions saturated with respect to Glauber's salt and ammonium sulphate or the double salt. For such solutions, the value of the molecular ratio of ammonium sulphate to sodium sulphate increases rapidly with rise of temperature until the ratio becomes equal to unity at the upper limit of the lower transition interval (20°). In view of the high value of the ratio at low temperatures, it is obviously possible to crystallise out a large proportion of the sodium sulphate from a solution containing sodium and ammonium sulphates by lowering the temperature.

Although Fig. 1 is well adapted to show the relationship between the double salt and the simple salts, the changes which occur on crystallisation may be more suitably discussed in reference to the curves which are shown in Fig. 2. In this diagram, the composition of any solution is represented by a single point. The horizontal axis gives the number of molecules of sodium sulphate per 1000 molecules of water, and the vertical axis the number of molecules of ammonium sulphate per 1000 of water. In the construction of this diagram, the required data for the solubility of sodium sulphate and of ammonium sulphate in water have been taken from the tables given in Landolt-Börnstein-Meyerhoffer. The isothermal curves connecting the points on the sodium sulphate and ammonium sulphate axes pass through the points which correspond with the saturated solutions recorded in table II. Below −16° and above 59·3°, the isothermals consist of two branches, and between these temperatures there are three branches on each isothermal. The isothermals actually represented on the diagram are those for −10°, 0°, 15°, 20°, 26·5°, 40°, 50°, 59·3°, 75°, and 100°. The sodium sulphate curves corresponding with the five highest temperatures are only indicated in so far as they do not interfere with the clearness of the diagram. The points *B*, *C*, and *D* correspond with the three invariant systems at −16°, 26·5°, and 59·3°, and are indicated by the same letters in Fig. 1.

The dotted curve *BD* represents the solutions which are saturated with respect to ammonium sulphate and double salt, *BC* those

FIG. 2.

Na_2SO_4—$(NH_4)_2SO_4$—H_2O.



which are saturated with respect to Glauber's salt and double salt, and *CD* those saturated with respect to anhydrous sodium sulphate and double salt. The region enclosed by the three curves corresponds with solutions which are saturated only with respect to the double salt.

By reference to Fig. 2, it is possible to predict what will occur when any solution containing sodium and ammonium sulphates is crystallised either by the removal of water at constant temperature or by a lowering of the temperature of the solution.

The diagram shows that the isothermal for 26·5° represents the maximum extension of the double salt curve, the molecular ratio of ammonium sulphate to sodium sulphate in the saturated solution varying from 5·2 when saturation with respect to ammonium sulphate is reached to 0·50 when the solution becomes saturated with respect to sodium sulphate. From this it is apparent that, at this temperature, the double salt may be crystallised out from solutions of widely varying composition. On proceeding from 26·5° to higher or lower temperatures, the double salt isothermals undergo a gradual contraction until they disappear at −16° and 59·3° respectively.

From the position of the dotted boundary curves on the diagram, it is evident that the solutions from which the double salt crystallises out between these limiting temperatures contain, in general, an excess of ammonium sulphate. At low temperatures, the required excess of ammonium sulphate is considerable, and for the most part solutions of the two sulphates when crystallised at low temperatures yield Glauber's salt as the solid product. If the concentration of the solution of the mixed sulphates is appropriately adjusted, a large proportion of the sodium sulphate may be removed in the form of Glauber's salt by cooling. Since the separation of Glauber's salt from the solution involves the removal of ten molecules of water for each molecule of sodium sulphate, it follows that the crystallisation will be accompanied by an automatic increase in the concentration of the ammonium sulphate.

The solubility data which determine the extent to which the separation of sodium and ammonium sulphates may be effected by crystallisation of Glauber's salt are recorded in table III for temperatures of −10·0° and −15·0°. The successive columns give the temperature, the nature of the solid phases, the molecular composition of the solution in terms of 1000 molecules of water, and the molecular ratio of ammonium sulphate to sodium sulphate in the saturated solution. The data cover the entire range of the Glauber's salt curves at the two temperatures, and by plotting the results it is possible to obtain the ratio of ammonium sulphate to

sodium sulphate in any solution which is saturated with respect to Glauber's salt at these temperatures.

TABLE III.

Temperature.	Nature of solid phases.	Molecules salt per 1000 mols. H_2O. Na_2SO_4.	$(NH_4)_2SO_4$.	Mol. ratio $\frac{(NH_4)_2SO_4}{Na_2SO_4}$.
−10·0°	Ice and Glauber's salt	7·32	47·2	6·45
−10·0	Glauber's salt	7·95	52·0	6·54
−10·0	„ „	8·51	60·4	7·10
−10·0	Glauber's salt and double salt	9·86	76·5	7·76
−15·0	Ice and Glauber's salt	7·48	69·7	9·3
−15·0	Glauber's salt	7·53	76·0	10·1
−15·0	Glauber's salt and double salt	7·20	84·0	11·7

The numbers in the last column show that the molecular ratio of ammonium sulphate to sodium sulphate in the solutions saturated with respect to Glauber's salt increases with increase in the ammonium sulphate content. Taking the value of the molecular ratio which corresponds with the middle portion of the isothermal, it follows that crystallisation at −10·0° will yield a mother liquor containing about seven molecules of ammonium sulphate per molecule of sodium sulphate, and at −15° a mother liquor containing ten to eleven molecules of ammonium sulphate per molecule of sodium sulphate.

If such mother liquors are evaporated at or about 100°, a large proportion of the ammonium sulphate present may be obtained in a pure condition. By reference to table II, it will be found that the solution saturated with respect to sodium sulphate and ammonium sulphate at 100° has the molecular composition

$$1000H_2O : 48{\cdot}0Na_2SO_4 : 129{\cdot}5(NH_4)_2SO_4.$$

For this solution, the molecular ratio of ammonium to sodium sulphate is equal to 2·7. If, therefore, we have a mother liquor for which, as a result of the separation of Glauber's salt by cooling to −15°, the molecular ratio of ammonium to sodium sulphate has been increased to 10·5 (compare table III), it follows that $\frac{10{\cdot}5-2{\cdot}7}{10{\cdot}5}\times 100$ = approximately 75 per cent. of the contained ammonium sulphate may be obtained in pure condition by evaporation at 100°.

The relations exhibited by the equilibrium conditions at low temperatures and in the neighbourhood of 100° have been made the basis of a method for the production of ammonium sulphate and Glauber's salt by the treatment of solutions of the mixed sulphates such as are obtained when nitre cake or mixtures of

nitre cake and sulphuric acid are employed for the absorption of ammonia (Brit. Patent 114236, 1918). In this process, the liquor from the ammonia saturator has its concentration suitably adjusted, and is then cooled to about $-10°$, at which temperature a considerable proportion of the sodium sulphate separates out in the form of Glauber's salt. The mother liquor is then transferred to an evaporator, and on evaporation of the solution, crystals of ammonium sulphate are deposited until the molecular ratio of ammonium sulphate to sodium sulphate in the hot liquid has been reduced to a value not less than about 2·7. The residual liquor is then suitably diluted and returned to the refrigerator in admixture with a further quantity of solution from the saturator.

In view of the fact that the liquid from the saturator inevitably contains a certain amount of free acid, it was of some interest to investigate the influence of the presence of free sulphuric acid on the crystallisation of Glauber's salt at low temperatures. In these experiments, solutions containing fixed quantities of sodium sulphate and ammonium sulphate and variable quantities of free sulphuric acid were cooled to $-10·0°$, and the composition of the mother liquors was determined. The results obtained are recorded in table IV, in which the composition by weight and the molecular composition of the resulting solutions are shown, in addition to the value of the molecular ratio of ammonium sulphate to sodium sulphate.

TABLE IV.

	Grams per 100 of water.			Molecules per 1000 of water.			Mol. ratio $\frac{(NH_4)_2SO_4}{Na_2SO_4}$.
	Na_2SO_4.	$(NH_4)_2SO_4$.	H_2SO_4.	Na_2SO_4.	$(NH_4)_2SO_4$.	H_2SO_4.	
a	6·19	38·05	—	7·85	51·9	—	6·61
b	6·48	37·9	3·98	8·21	51·7	7·31	6·30
c	6·61	37·7	7·95	8·38	51·4	14·6	6·13

Although the ratio of ammonium sulphate to water in the three mother liquors is not quite the same, the values are sufficiently close to permit of a comparison of the effect of the free acid on the separation of the Glauber's salt, and it is evident from the table that the molecular ratio of ammonium sulphate to sodium sulphate in the solution decreases as the proportion of free acid increases. In other words, the separation of Glauber's salt is less complete in the presence of free acid, but the influence of the acid is not such as to affect seriously the efficiency of the cooling process. It may be noted that the mother liquor in experiment *c* contains about 5·2 per cent. of free sulphuric acid.

With regard to the influence of free acid on the separation of

ammonium sulphate by evaporation of the mother liquor obtained in the previous cooling process, it has been found that the molecular ratio of ammonium sulphate to sodium sulphate, which is characteristic of the acid-free solution when saturated with respect to sodium and ammonium sulphates at 100°, is not appreciably altered in the presence of a considerable quantity of free acid.

An experiment in which this ratio was determined in the presence of free sulphuric acid may be quoted. Fifty grams of a sulphuric acid solution of the approximate molecular composition, $1000H_2O:100H_2SO_4$, were placed in a tube provided with a stirrer and heated at 100°. Excess of finely powdered sodium and ammonium sulphates was added, and the mixture stirred for about an hour, when a sample of the solution was found to have the molecular composition,

$$1000H_2O:79{\cdot}6Na_2SO_4:224{\cdot}7(NH_4)_2SO_4:105{\cdot}4H_2SO_4.$$

The molecular ratio of ammonium to sodium sulphate in the saturated solution, which, it may be noted, contains about 15 per cent. of free acid, is thus 2·8, whilst the value of this ratio for the acid-free solution is 2·7.

The results of the observations in acid solutions lead to the conclusion that the presence of free acid in moderate quantities does not affect to more than a small extent either the separation of Glauber's salt by crystallisation at low temperatures or the separation of ammonium sulphate by evaporation of the resulting mother liquor.

Summary.

The equilibrium relations in the ternary system Na_2SO_4–$(NH_4)_2SO_4$–H_2O between −20° and 100° are described and illustrated by diagrams.

The characteristic features of the system are in a large measure determined by the double salt $Na_2SO_4,(NH_4)_2SO_4,4H_2O$, which is formed from Glauber's salt and ammonium sulphate at −16°, and decomposes with the formation of the anhydrous simple salts at 59·3°.

Between −16° and 20°, the double salt is decomposed by water with the formation of Glauber's salt, and between 41·5° and 59·3° it is decomposed with the formation of anhydrous sodium sulphate.

The temperature at which Glauber's salt is transformed into the anhydrous sulphate is depressed to 26·5° by the addition of ammonium sulphate. At this temperature, the solution formed is in equilibrium with Glauber's salt, anhydrous sodium sulphate, and the double salt.

It is shown that sodium sulphate and ammonium sulphate may

be separated from one another by subjecting solutions of appropriate concentration to low temperatures, when most of the sodium sulphate crystallises out in the form of Glauber's salt. A large proportion of the ammonium sulphate in the mother liquor may be obtained in pure condition by evaporation at 100°.

The method of separation is not appreciably affected by the presence of moderate quantities of free sulphuric acid.

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LIX.—*Acylated* p-*Phenylenemethyldiamines.*

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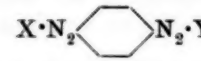
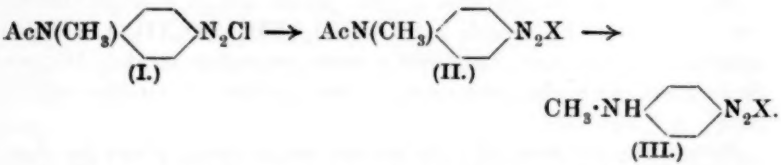
THE acyl derivatives of *p*-phenylenediamine have long had considerable technical importance, owing to the circumstance that these derivatives afford a practicable method of diazotising this diamine in both its amino-groups, a process required in the manufacture of bisazo-colouring matters containing the complex:



It has also been found that the monodiazonium salts (I) of the acyl derivatives of *p*-phenylenemethyldiamine are utilisable in the production of aminoazo-dyes (III), the acyl group being removed by hydrolysis from the intermediate product, which has the general formula II:



In certain cases, the acylaminoazo-compounds themselves are found to have useful tinctorial properties (Morgan and Micklethwait, *J. Soc. Dyers*, 1909, **25**, 107; Farbenfabriken vorm. F. Bayer & Co., D.R.-P. 296964).

The *p*-aminomethylacylanilides can be prepared by the following methods:

(i) From methylaniline, by successively acylating this base, nitrating its acyl derivative, and reducing the *p*-nitro-compound.

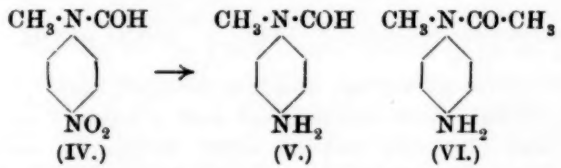
(ii) By methylating the acylanilide and then subjecting the methylacylanilide to the same treatment as in method (i).

(iii) Successive methylation and acylation of *p*-nitroaniline, followed by reduction of the resulting *p*-nitromethylacylanilide.

(iv) Methylation of the alkali derivative of 4:4′-dinitrodiazoaminobenzene, and hydrolysis of the methylated diazoamine to a mixture of chlorobenzene and methyl-*p*-nitroaniline, the secondary nitro-base being then acylated and reduced (Morgan and Alcock, T., 1909, **95**, 1332).

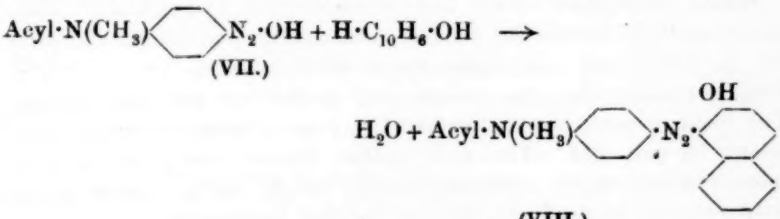
Of these four methods, the first is generally the most practicable providing that methylaniline is available in sufficient amount. Being in possession of considerable quantities of this base obtained by the process indicated in English Patent 514 of 1916, the authors have utilised this means of preparing several intermediate compounds from methylaniline which have not hitherto been described (Eng. Pat. 16520 of 1916).

p-*Nitromethylformanilide* (IV) is obtainable by nitrating methylformanilide, this acyl derivative being readily prepared by warming methylaniline with concentrated formic acid. It was shown that in the main product of this nitration the nitro-group enters the para-position with respect to the acylamino-complex, this orientation being demonstrated by hydrolysing the nitro-compound to *p*-nitromethylaniline and by converting this secondary base into its characteristic nitrosoamine.



(IV.) (V.) (VI.)

p-*Aminomethylformanilide* (as-*formyl*-p-*phenylenemethyldiamine*) (V) results from the reduction of the new nitro-derivative. Methylacetanilide, readily obtainable by mixing together methylaniline and acetic anhydride, is successively converted into *p*-nitromethylacetanilide and p-*aminomethylacetanilide* (as-*acetyl*-p-*phenylenemethyldiamine*) (VI). These two *p*-aminomethylacyl-



(VIII.)

anilides when treated with nitrous anhydride in dry acetone solution give rise to diazohydroxides (VII), which combine readily with dry β-naphthol, the condensation being accompanied by the elimination of a molecular proportion of water.

The *acylmethylaminobenzeneazo-β-naphthols* (VIII) thus produced are identical with the products obtained by successively diazotising the *p*-aminomethylacylanilides in aqueous solution and combining the diazonium salt with alkaline β-naphthol.

The foregoing diazohydroxides are obtainable as colourless, amorphous solids soluble in acetone and insoluble in ether or water.

p-Aminomethylbenzanilide and *p*-aminoethylbenzanilide when subjected to the action of nitrous anhydride in acetone solution yield only oily diazo-derivatives (compare Morgan and Alcock, *loc. cit.*).

Experimental.

I. p-*Aminomethylformanilide and its Acetyl Homologue.*

The starting point in these preparations was methylaniline, prepared by treating aniline with formaldehyde in the presence of zinc dust and sodium hydroxide (Eng. Pat. 514 of 1916). Methylformanilide was produced by heating the secondary base with one part of concentrated commercial formic acid for eight hours, and obtained as a viscid oil, which was extracted with benzene.

p-*Nitromethylformanilide*, $NO_2C_6H_4N(CH_3)\cdot COH$.—Methylformanilide (three parts) was dissolved in eight parts of cold concentrated sulphuric acid and nitrated with a mixture of two parts of nitric acid (D 1·42) and an equal volume of concentrated sulphuric acid. The nitration was carried out at 0° to 10°, and the product poured on ice. The pale yellow precipitate was crystallised from alcohol, when it separated in pale yellow, prismatic crystals melting at 118—120°:

0·1643 gave 23·2 c.c. N_2 at 20° and 752 mm. N = 16·03.

$C_8H_8O_3N_2$ requires N = 15·55 per cent.

When hydrolysed with hot concentrated hydrochloric acid, *p*-nitromethylformanilide yielded successively *p*-nitromethylaniline (m. p. 152°) and *p*-nitrophenylmethylnitrosoamine (m. p. 100°), thus demonstrating the orientation of the entrant nitro-group. The yield of *p*-nitromethylformanilide from a series of batches was about 70 per cent. The acid mother liquors slowly deposited a more readily soluble nitro-compound, which, being contaminated with resinous by-products, was not further investigated.

p-*Aminomethylformanilide* (as-*Formyl*-p-*phenylenemethyldiamine*).—*p*-Nitromethylformanilide (10 grams) was added gradually to a mixture of 10 grams of iron filings, 0·5 gram of formic acid, and 30 c.c. of water at 50°. The mixture was agitated vigorously, and the temperature, which tended to rise rapidly after each addition, was not allowed to exceed 75°. After the addition of all the nitro-compound, the heating was continued at this temperature for a few minutes, and the mixture was then treated with an excess of calcium carbonate and filtered quickly while hot. The *p*-aminomethylformanilide separated in feathery needles on cooling, and a further crop was obtained from the washings of the residue concentrated in a stream of carbon dioxide. The crude product was crystallised from water, separating therefrom in grey needles melting at 129—130°:

0·2213 gave 35·4 c.c. N_2 at 19° and 761 mm.* N = 18·68.

$C_8H_{10}ON_2$ requires N = 18·66 per cent.

p-Aminomethylformanilide was obtained by crystallisation from light petroleum in colourless needles melting at 132°. It darkened on exposure to light and air, especially when in a moist condition.

p-*Aminomethylacetanilide*.—Methylacetanilide was prepared by adding acetic anhydride (30 grams) to an equal weight of methylaniline. Much heat was generated, and, after cooling, the solution was poured into an equal volume of water. The acetyl compound remained oily for several days, but was caused to solidify by mixing with 2 c.c. of concentrated ammonia solution.

Methylacetanilide (m. p. 100°), recrystallised from alcohol, was dissolved in four parts of concentrated sulphuric acid and nitrated at 0° to 12° with 1·3 parts of nitric acid (D 1·42) mixed with an equal volume of concentrated sulphuric acid. The product obtained by pouring the solution on ice and crystallisation from alcohol melted at 153°. It was reduced by the method already described in the case of the formyl derivative (above).

p-Aminomethylacetanilide separated in brown needles, and was purified by crystallisation from hot water, when it was obtained in greyish-white needles melting at 60°:

0·1320 gave 18·4 c.c. N_2 at 19° and 768 mm. N = 16·39.

$C_9H_{12}ON_2$ requires N = 17·07 per cent.

Further crystallisation from light petroleum gave colourless needles of the base melting at 63°. On exposure to air, the base assumed a yellow colour.

* In this and subsequent analyses the nitrogen was measured over potassium hydroxide (50 grams in 100 grams of water).

II. *Diazo-derivatives of* p-*Aminomethylacylanilides.*

Formylmethylaminobenzene-4-diazohydroxide.—A solution of *p*-aminomethylformanilide in dry acetone (twenty-five parts) was cooled to −10° and treated with excess of nitrous anhydride dissolved in the same solvent. The diazo-compound, which was obtained as a greyish-white, granular precipitate by the addition of cooled dry ether, darkened rapidly on exposure:

0·2060 gave 41·8 c.c. N_2 at 22·5° and 767 mm. N = 23·55.
$C_8H_9O_2N_3$ requires N = 23·46 per cent.

This product after drying over quicklime in a partial vacuum decomposed violently at 131—132°. When mixed with dry β-naphthol, the desiccated diazohydroxide combined to form an azo-derivative with loss of water, the mixture becoming damp.

Acetylmethylaminobenzene-4-diazohydroxide.—The foregoing treatment with nitrous anhydride applied to *p*-aminomethylacetanilide led to the production of a colourless, granular deposit of diazohydroxide precipitated by ether from the acetone solution. The product on exposure to air and light assumed a pale yellow colour:

0·2018 gave 38·8 c.c. N_2 at 22° and 766 mm. N = 22·30.
$C_9H_{11}O_2N_3$ requires N = 21·76 per cent.

The dried diazohydroxide decomposed violently at 131—132°, and when triturated with β-naphthol it combined to form an azo-derivative, water being eliminated.

Comparative experiments on the diazotisation of *p*-aminomethylbenzanilide and *p*-aminoethylbenzanilide with nitrous anhydride in acetone led only to oily diazo-derivatives which formed azo-compounds with β-naphthol and similar phenolic substances (compare Morgan and Alcock, T., 1909, **95**, 1323).

III. *Azo-derivatives of* p-*Aminomethylformanilide and* p-*Aminomethylacetanilide.*

Formylmethylaminobenzene-4-azo-β-naphthol,
$COH{\cdot}N(CH_3){\cdot}C_6H_4{\cdot}N_2{\cdot}C_{10}H_6{\cdot}OH$.
—This compound was prepared by direct combination between formylmethylaminobenzene-4-diazohydroxide and dry β-naphthol or from the diazonium chloride of *p*-aminomethylformanilide prepared in aqueous solution and combined with alkaline β-naphthol. The azo-β-naphthol separated as a dark purple solid, insoluble in

aqueous alkalis, but dissolving in alcohol to a magenta solution. It separated from this solution in ill-defined crystals, which, after washing with ether, melted at 160—161°:

0·1426 gave 17·3 c.c. N_2 at 25° and 763 mm. N = 13·81.
$C_{18}H_{15}O_2N_3$ requires N = 13·76 per cent.

p-Aminomethylformanilide was diazotised and combined with the following phenolic substances: salicylic acid, α-naphthol-4-sulphonic acid (N and W acid), and 8-amino-α-naphthol-3:6-disulphonic acid (H acid), giving rise to a series of azo-dyes, the properties of which are tabulated below.

Azo-derivatives of p-*Aminomethylacylanilides.*

Base.	Phenolic compound.	Colour.	Azo-dye. Dyeing effect on wool (*a*) and silk (*b*).		Colour with concentrated sulphuric acid.
			a.	*b*.	
p-Aminomethylformanilide.	Salicylic acid	orange-brown powder.	brownish-yellow	lemon-yellow	orange-brown
	β-Naphthol	ill-defined dark red nodules			crimson
	"N & W" acid	dark red powder	russet brown	brownish-red	reddish-brown.
	"H" acid	deep purple powder	brownish-purple	"royal" purple	dark brownish-red, crimson on dilution.
p-Aminomethylacetanilide.	Salicylic acid	brownish-yellow powder	greenish-yellow	golden-yellow	bright orange-brown
	β-Naphthol	well-defined red needles			bright crimson
	"N & W" acid	orange-red powder	scarlet	scarlet	reddish-brown
	"H" acid	purple powder	bluish-purple reddened by meta-chrome mordant	"Bordeaux" red	crimson

Acetylmethylaminobenzene-4-azo-β-naphthol,

$$CH_3\cdot CO\cdot N(CH_3)\cdot C_6H_4\cdot N_2\cdot C_{10}H_6\cdot OH.$$

—This azo-derivative was obtained by grinding together acetylmethylaminobenzene-4-diazohydroxide and β-naphthol; the mixture rapidly turned red and became moist owing to the elimination of water due to the azo-condensation. It was also prepared by diazotising *p*-aminomethylacetanilide in cold concentrated hydrochloric acid, the solution of the soluble diazonium chloride being added to alkaline β-naphthol. The product crystallised from alcohol in well-defined, transparent, red tablets or flattened needles melting at 139°:

0·1414 gave 16·1 c.c. N_2 at 17° and 766 mm. N = 13·34.

$C_{20}H_{17}O_2N_3$ requires N = 13·15 per cent.

p-Aminomethylacetanilide was also combined with several other phenolic substances, giving rise to the above azo-dyes.

The authors desire to express their thanks to Mr. A. W. H. Upton, A.C.G.F.C., for assistance in the preliminary experiments of this investigation.

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LX.—*The Constitution of Carbamides. Part VII. The Mechanism of the Synthesis of Urea from the Interaction of Carbonyl Chloride and Ammonia. Part VIII. The Formation of Urea and of Biuret from Oxamide*

By Emil Alphonse Werner and (Part VIII.) George Kingsford Carpenter.

The formation of urea from the interaction of carbonyl chloride and ammonia has been generally considered to be a direct change analogous, for example, to the formation of acetamide from the interaction of acetyl chloride and ammonia. For this reason, this synthesis of urea is invariably set forth as 'conclusive' evidence of the 'carbamide' formula. This is mainly due to the fact that the so-called secondary products have been ignored, so far as their bearing on the mechanism of the change is concerned. Given the consideration they deserve, they clearly indicate the true origin of

urea in this reaction, which in truth is no more than Wöhler's synthesis in another form.

Natanson (*Annalen*, 1856, **98**, 287) first isolated urea from this reaction, Regnault (*Ann. Chim. Phys.*, 1838, [ii], **69**, 180) having obtained indications of its formation.

Bouchardat (*Compt. rend.*, 1869, **69**, 961) showed that cyanuric acid and ammelide were formed in addition to urea; Fenton (T., 1879, **35**, 793) suggested that urea was possibly the result of a secondary reaction, on account of the small proportion obtained. Hantzsch and Stuer (*Ber.*, 1905, **38**, 1041, 2326) found cyamelide as an additional product when ammonia was passed into a solution of carbonyl chloride in light petroleum at 0°. This fact is of interest, since it confirms the author's theory of the constitution and polymerisation of cyanic acid (T., 1913, **103**, 1017).

Origin of Urea, and Formation of Biuret in the Interaction of Carbonyl Chloride and Ammonia.

If urea had the 'carbamide' structure, there appears no reason why it should not be formed in quantitative yield without the accompaniment of several secondary products. In view of the evidence, it is remarkable that no explanation of this has yet been suggested.

The cause undoubtedly lies in the recognition of the fact that there exists no tendency to the formation of a compound containing the system $:C(NH_2)_2$, since this cannot form a part of a stable molecule (this vol., p. 624).

It is evident that the formation of cyanuric acid and of cyamelide arises from the polymerisation of cyanic acid ($HOCN \rightleftharpoons HN{:}CO$), generated according to the scheme:

$$CO\langle_{Cl}^{Cl} + 2NH_3 \longrightarrow CO\langle_{Cl}^{NH_2}\ (NH_4Cl) \longrightarrow HCl + \begin{matrix} HOCN \longrightarrow \text{Cyamelide} \\ \uparrow\downarrow \quad \text{by polymerisation} \\ HN{:}CO \longrightarrow \text{Cyanuric acid.} \end{matrix}$$

Cyanic acid being generated in the presence of ammonia, the origin of urea in this synthesis is self-evident. In support of this explanation of the change, it was found that biuret constituted a large part of the secondary products, since it was shown (T., 1913, **103**, 1014, 2278; P., 1914, **30**, 262) that whilst biuret is formed from the union of cyanic acid and urea, ammelide is formed from the interaction of cyanic acid and biuret. It is not surprising that the formation of the latter has been overlooked by previous investigators, since there was no reason to expect its production according to the usual, but incorrect, view of the change.

In order to place on record information as regards the relative proportions of the different products formed, a quantitative study of the reaction at different temperatures has been made.

The following results were obtained after passing a current of dry ammonia into a 3 per cent. solution of carbonyl chloride in benzene until decomposition was completed:

	Expt. I.	Expt. II.	Expt. III.
Temperature	20—25°	40—50°	65—70°
Products formed	Per cent.	Per cent.	Per cent.
Urea	31·7	37·3	41·2
Biuret	14·4	10·1	7·8
Ammelide	7·65	8·6	10·6
Cyanuric acid	3·45	6·4	5·98
Cyamelide	0·69	trace	none

The results are expressed in proportion to the respective theoretical yields, calculated on the following bases: thus $COCl_2$ = one mol. each of urea, cyanuric acid, and cyamelide, since the two latter are formed from the polymerisation of cyanic acid, $2COCl_2$ = one mol. of biuret, and $3COCl_2$ = one mol. of ammelide.

It will be noticed that in Expts. I and II biuret constitutes the chief product after urea, and whilst the yield falls with rise of temperature, that of ammelide increases, since, in agreement with theory (*loc. cit.*), the formation of the latter from its precursor biuret is promoted at the higher temperature. The conditions being unfavourable for the existence of free cyanic acid, the proportion of cyanuric acid generated was consequently small.

After the crude product from Expt. I had been shaken with a small quantity of pure alcohol, ethyl allophanate (=5·3 per cent. of the theoretical) was extracted from the benzene–alcohol filtrate. This could only have resulted from a reaction with cyanic acid generated from the substance, $NH_2 \cdot COCl$, present in the original product, thus, $2NH_2 \cdot COCl + C_2H_5 \cdot OH = C_4H_8O_3N_2 + 2HCl$.

Whilst the total chlorine content of the carbonyl chloride was accounted for as ammonium chloride and a small quantity of chloroformamide, it will be seen, from the sum of the other products, taking an average for the three experiments, that only about 62 per cent. of the carbonyl group was recovered. The deficiency was due to decomposition of carbonyl chloride by water generated simultaneously with the formation of ammelide, thus:

$$HN\langle^{CO\cdot NH_2}_{CO\cdot NH_2} + OC{:}NH \longrightarrow HN\langle^{CO\cdot NH}_{CO\cdot NH}\rangle C{:}NH + H_2O.$$

When ammonia dissolved in benzene was added to an excess of carbonyl chloride in the same solvent (ratio, $COCl_2 + 2NH_3$), the yield of urea was equal to only 4·6 per cent. of the theoretical. Cyamelide and cyanuric acid were formed in appreciable amount;

biuret and ammelide were absent. Whilst much carbonyl chloride was unchanged, the solution contained 19 per cent. of the theoretical yield of the compound, $NH_2 \cdot COCl$ (Expt. IV).

Bouchardat's (*loc. cit.*) conclusion that guanidine was formed in this reaction could not be confirmed.

In support of the author's contention as regards the system $:C(NH_2)_2$, and in confirmation of the present theory of the formation of urea in this reaction, it may be pointed out that thiourea is not formed from the interaction of ammonia and thiocarbonyl chloride. The fact that ammonium thiocyanate is produced instead supplies a convincing argument.

Experimental.

The following method was adopted in obtaining the results given under Expts. I, II, and III: 12 grams of carbonyl chloride dissolved in 400 c.c. of freshly distilled benzene were placed in a stout, wide-mouthed bottle provided with a cork which carried a delivery tube, thermometer, and exit tube. A slow current of dry ammonia (generated as described later) was delivered on to the surface of the liquid, which was kept continually agitated. On account of the rather gelatinous form of the product, it was scarcely possible to ensure uniformity in the progress of the reaction or to maintain a constant temperature. In Expt. I, the vessel was immersed in water at 0°, in Expt. II in water at 15°, in Expt. III no artificial cooling was used. The higher temperature given represents the maximum attained during the progress of each experiment.

The details of Expt. I will suffice to illustrate how the different products were estimated.

The solid material, after being washed with benzene, was collected, dried, and extracted with warm alcohol; the residue 12·04 grams of ammonium chloride present), on treatment with water, left 0·436 gram of insoluble matter, from which 0·4 gram of ammelide was extracted by solution in sodium hydroxide. Hence cyamelide present = 0·036 gram. The alcoholic extract was concentrated by evaporation to a small volume; 2·25 grams of crystalline matter (*A*) separated after cooling, and the mother liquor on evaporation to dryness left a residue (*B*) = 2·45 grams.

Product (*A*) contained 0·96 gram of ammonium chloride and 0·95 gram of urea; cyanuric acid was absent, and the remainder (0·34 gram) was chiefly ethyl allophanate with a trace of biuret. Product (*B*) was dissolved in 50 c.c. of water. Cyanuric acid was estimated in an aliquot portion by titration with *N*/10-sodium

hydroxide, using phenolphthalein as indicator: required for total, 14 c.c. $N/10$-NaOH = 0·18 gram $C_3H_3O_3N_3$.

Biuret was estimated colorimetrically, as previously described (T., 1913, **103**, 2282). Found, 0·897 gram; it was also separated in crystalline form and identified (m. p. 192°).

Urea was estimated in this solution by precipitation as nitrate, which was washed with ether, dried, and weighed.

Urea found = 1·36. Hence total urea $(A)+(B)$ = 2·31 grams = 31·7 per cent. of the theoretical amount from 12 grams of carbonyl chloride.

Since guanidine can be detected with ease, even in a 0·1 per cent. solution and in the presence of urea, and of biuret by means of picric acid, its absence was proved by the negative result obtained with this reagent.

Expt. IV.—Interaction of Carbonyl Chloride and Two Molecular Proportions of Ammonia.—To 4 grams of carbonyl chloride in 100 c.c. of benzene, 0·68 gram of ammonia dissolved in 200 c.c. of benzene was added.

The precipitated material was washed with benzene, collected, dried, and extracted with alcohol. The amount of urea found in the resulting solution, after removal of ammonium chloride, was 0·0278 gram = 4·6 per cent. of the theoretical. The benzene filtrate was shaken with a slight excess of pure sodium hydroxide solution, to which, after neutralisation, an excess of silver nitrate was added. The washed precipitate of silver chloride and silver cyanate was digested with dilute nitric acid to remove the latter salt. The resulting solution required, for precipitation of the silver, 76·8 c.c. of $N/10$-potassium thiocyanate, equal to 19 per cent. of the theoretical amount of the compound, $NH_2{\cdot}COCl$, present in the benzene solution; thus $NH_2{\cdot}COCl + 2NaOH = NaOCN + NaCl + 2H_2O$.

Note on a Convenient Method for obtaining a Continuous Current of Dry Ammonia without the Application of Heat.

The following method has given admirable results, and it seemed worth while to place it on record. It is adaptable to any scale, and where, for example, it was required to saturate 8 litres of alcohol with dry ammonia, the procedure was as follows.

Ammonia solution (D 0·880) was allowed to drop from a separating funnel at a regulated rate on 400 grams of commercial sodium hydroxide, in coarse powder, contained in a round-bottomed flask of about 4 litres capacity. The gas was rapidly liberated,

and the temperature of the mixture gradually fell to nearly zero. The process required no attention beyond occasionally replenishing the supply of ammonia solution; nearly 90 per cent. of the ammonia from 1500 c.c. of the concentrated solution was obtained without any application of heat. In order to avoid interference with the continuity of the process through the effects of back pressure, it was necessary to connect the limb of the separating funnel with a short length of glass tubing drawn out to an aperture of about 0·5 mm., whereby the necessary hydrostatic pressure was maintained.

Summary.

(1) The synthesis of urea from the interaction of carbonyl chloride and ammonia does not supply evidence in support of the 'carbamide' formula.

(2) A quantitative study of the interaction, and the nature and number of the secondary products, has shown that urea is produced from the union of ammonia and cyanic acid (in the keto-form), generated from the decomposition of the compound, $H_2N{\cdot}COCl$, produced in the first instance.

(3) It is shown, for the first time, that biuret is a product of this reaction.

Part VIII.—The Formation of Urea and of Biuret from Oxamide. [With George Kingsford Carpenter.]

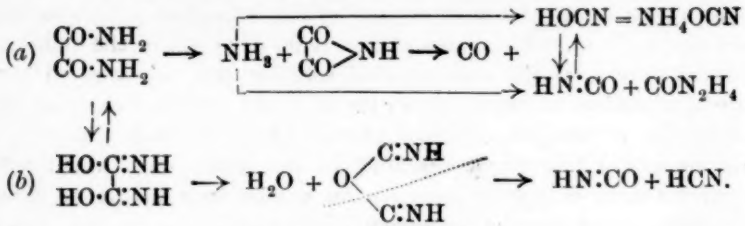
Many years ago, Williamson (*Memoir, Congrès. Scientif. de Venise*, 1847 *) obtained urea by heating a mixture of oxamide and mercuric oxide. This has been accepted as evidence of a close connexion in constitution between urea and the diamide, the latter being supposed merely to lose a carbonyl group in the change.

An investigation of the mechanism of the formation of urea has shown, as expected, that mercuric oxide plays no part in its production; thus, when mixtures of oxamide and mercuric oxide in different proportions were heated to the temperature (230—240°) at which the oxide was completely reduced, no urea could be detected in the product (Expt. I).

When oxamide was heated to a temperature just sufficient to effect complete volatilisation, ammonium cyanate, urea, and biuret were found in the sublimate, whilst ammonia, water, carbon monoxide, and hydrogen cyanide were evolved.

* It was not possible to consult the original paper.

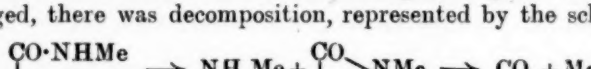
The decomposition is brought about as follows:



Since ammonia was first evolved (at about 110°) whether mercuric oxide was present or not, it is evident that the formation of urea from oxamide, in accordance with (*a*), is but another example of Wöhler's synthesis.

The respective yields of ammonium cyanate and of urea were 2·9 and 4·18 per cent. of the theoretical when oxamide was rapidly heated and the vapours quickly condensed by artificial cooling. When the amide was slowly heated without further precaution, the yields were 2·4 and 2·6 per cent. respectively, whilst the formation of hydrogen cyanide was more evident than in the former case (Expts. II, III, IV, and V). The formation of biuret is accounted for by the above explanation of the mechanism of the decomposition.

It may be mentioned that when *s*-dimethyloxamide was heated with mercuric oxide to 240°, no dimethylurea was formed; when the amide was heated alone, whilst the greater part volatilised unchanged, there was decomposition, represented by the scheme:



This change is being further investigated.

Experimental.

Expt. I.—An intimate mixture of 1·76 grams of oxamide and 4·32 grams of mercuric oxide was heated in a test-tube partly immersed in glycerol. Ammonia was evolved at 110°, and at 230—240° the colour of the mixture changed to grey and the heating was stopped. The cold residue was extracted with 10 c.c. of water, but no urea could be detected in the solution, even by means of the extremely delicate xanthhydrol test. The experiment was repeated, with different proportions of the two substances, with a similar result.

Expt. II.—Two grams of oxamide were heated in a hard glass tube held horizontally until the whole had sublimed. The sublimate

was extracted with cold water, and to the solution 10 c.c. of $N/10$-silver nitrate were added, 5·65 c.c. being required for the precipitation of the ammonium cyanate present, which was therefore equal to 2·49 per cent.

Expt. III.—The above experiment was repeated, but the forepart of the tube was cooled with a circular current of water; 6·8 c.c. of $N/10$-silver nitrate were required; hence 2·9 per cent. of the theoretical amount of ammonium cyanate was present.

Expts. IV and V.—Two grams of oxamide were heated as in Expt. II, the aqueous extract, after removal of 'cyanate,' being evaporated to dryness. The urea extracted by alcohol from the residue gave 6·66 c.c. N_2 at N.T.P. on decomposition with alkaline sodium hypobromite = 2·61 per cent. of the theoretical; 10·68 c.c. N_2 at N.T.P. were obtained from the urea produced under the conditions of Expt. III, which corresponds with 4·18 per cent. of the theoretical amount.

Summary.

(1) Urea is not formed when a mixture of oxamide and mercuric oxide is heated to the stage at which the oxide is completely reduced.

(2) The synthesis of urea from oxamide is the result of the generation of cyanic acid and ammonia from the decomposition of the amide.

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[*Received, July 18th*, 1918.]

LXI.—*A New Method for the Determination of Conductivity.*

By EDGAR NEWBERY.

THE convenience and simplicity of Kohlrausch's method for the determination of the conductivity of aqueous solutions has been so long recognised that at the present time no trustworthy data on this subject exist which have not been obtained by the above method or some slight modification of it.

Further, all conductivity vessels are standardised with the aid of the original values given by Kohlrausch for potassium chloride solutions.

A critical examination of the method shows, however, that it is

based on several assumptions which have not so far been experimentally proved correct. The following are the chief objections to the method.

(1) It is assumed that by using alternating current, all polarisation effects are eliminated.

Taylor and Acree (*J. Amer. Chem. Soc.*, 1916, **38**, 2396 *et seq.*) have studied this subject, and have shown that consistent results with simple electrolytes can only be obtained by using a perfect sine wave current and extrapolating the results thus obtained to determine the conductivity when the frequency is infinite. It appears probable, therefore, that with these precautions polarisation is absent in the case of simple electrolytes, such as potassium chloride, but when certain other electrolytes are used, especially with insufficiently platinised electrodes, it is by no means certain that decomposition of the electrolyte, with consequent polarisation of the electrodes, does not occur. To quote an extreme case, an alternating current passed between copper electrodes in a concentrated solution of potassium cyanide dissolves the copper with the same efficiency as direct current when the frequency is not greater than 1000 per minute, and with an efficiency of 33 per cent. when the frequency is 38,000 per minute. Since very small traces of polarisation may exert very great influence on the measured conductivity, it follows that grave doubt is thrown on the trustworthiness of many of our present conductivity data.

(2) It is assumed that conductivity is independent of current density, current concentration, and type of current (direct or alternating). Whilst this is probably true in general, it has not been sufficiently investigated to be relied on in all cases.

(3) Errors are introduced by self-induction, electrostatic capacity, shape of conductivity vessel, etc., the corrections for which are troublesome and of doubtful accuracy.

It is therefore very desirable to devise a method of measuring conductivity which will utilise direct current and completely eliminate the effect of polarisation at the electrodes.

Experimental.

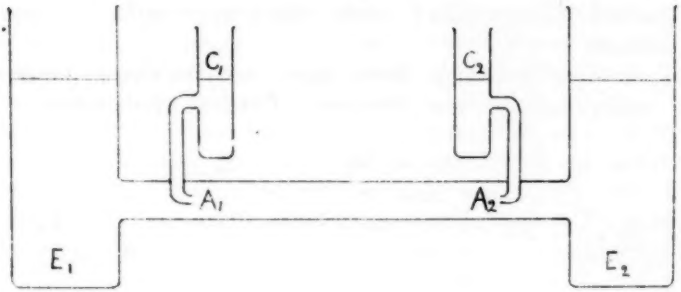
The method described is a simple modification of a common method for measuring the resistance of a metallic conductor by determining the fall of potential along it during the passage of a known current.

Altogether, seven different forms of the apparatus were constructed, but the principle of them all may be seen from Fig. 1, which shows the most convenient form for general use in obtain-

ing relative values, and Fig. 2, which shows the most accurate form for the determination of absolute values.

In using the first form of apparatus, a small but constant current is passed between the electrodes E_1E_2, along the tube A_1A_2, and also through a standard resistance. Standard electrodes (calomel, mercurous sulphate, etc.) are constructed in the vessels C_1C_2, and these are connected with an accurate dial potentiometer reading to five significant figures. The extremities of the standard resistance are also connected to the same potentiometer, and by means of a commutator, the fall of potential along the tube A_1A_2 and across the terminals of the standard resistance may be measured

FIG. 1.



in rapid succession. The specific conductivity of the electrolyte is then given by

$$K = \frac{D^2}{VR} \times \frac{y}{x},$$

where D is the distance between the electrode tips A_1A_2, V the volume of the liquid in the tube between the same points, R the standard resistance, and x and y the potential differences between the electrodes C_1C_2 and between the terminals of the standard resistance respectively. All measurements described were carried out with the apparatus immersed in a thermostat at 25°.

Conductivity of N*-Potassium Chloride at* 25°.

For this purpose, the apparatus shown in Fig. 2 was used. A burette (50 c.c.) was chosen out of a large number such that the graduations were as uniform as possible, and carefully calibrated by a weighing method with mercury, the exact distance between the first and last markings being determined with the cathetometer. (These measurements were repeated after construction of the apparatus.) The tap was then cut off, standard electrode

vessels were sealed on as shown, with the tips central and exactly opposite the end graduations, and large side-tubes, B_1B_2, sealed on well behind the electrode tips. These side-tubes were connected with the main electrode vessels E_1E_2.

Errors due to expansion of the glass, irregularities in the tube, etc., were calculated and found to amount to not more than 0·001 per cent.

The electrodes used in all four vessels were calomel, great care being taken to secure purity of mercury and calomel. Before use, the electrodes C_1C_2 were connected through a sensitive galvanometer. If any deflexion was observed, they were short-circuited for some time until no difference of potential could be detected.

The main electrode vessels were 8 cm. high and 5 cm. in diameter, the mouths being closed with well-fitting corks to prevent evaporation.

The standard resistance, 99·84 ohms, and the thermometer used were calibrated at the National Physical Laboratory. The

FIG. 2.

galvanometer was a moving coil instrument sensitive to 10^{-9} ampere.

By varying the strength of the main current between 0·1 and 5 milliamperes, readings were taken on very varied portions of the potentiometer.

By repeatedly changing the direction of the main current, errors due to concentration changes in the electrolyte and inequality of potential between C_1 and C_2 were eliminated. By experiments with other forms of the apparatus, using different lengths of tube and different sized electrode tips, it was found that errors due to uneven flow of current in the immediate neighbourhood of the electrode tips are not greater than 0·01 per cent. if the diameter of these tips is not more than 0·1 of that of the main tube.

The chief difficulty experienced in all these experiments lay in securing a perfectly constant main current. The use of calomel electrodes of large area and small currents was so far successful in this case in overcoming this difficulty that long series of closely agreeing results were easily obtained. Other devices for the same purpose are described later.

Purification of Materials.—The water was redistilled, using a tin condenser, and had a conductivity of $0{\cdot}5 \times 10^{-6}$ mhos.

The mercury was redistilled and sprayed through dilute nitric acid several times before use.

The calomel was washed with water and well triturated with mercury and potassium chloride solution several times before being placed in the apparatus.

The potassium chloride was a special product, guaranteed pure by the manufacturers. This was precipitated from a saturated solution by means of hydrogen chloride, dried, and heated to dull redness, and again precipitated from a hot saturated solution in conductivity water by rapid cooling. After drying and heating to dull redness, it was weighed out and the solution made up at 18° to the strength used by Kohlrausch (74·59 grams per litre at 18°). This solution was made up, *ab initio*, three times, starting with different samples of the original salt, and no difference in conductivity could be detected in the three solutions.

The solution was exactly neutral to indicators, and no trace of sulphate, carbonate, phosphate, or nitrate could be detected by the usual tests. Quartz vessels were used wherever possible in the preparation of the salt, and all glass vessels were well steamed out shortly before use to avoid the introduction of sodium silicate. The flame spectrum showed the sodium lines somewhat feebly, but no other ingredient. Since the presence of as much as 1 per cent. of sodium chloride in the potassium salt would only raise the conductivity of the solution by 0·05 per cent., it is improbable that any appreciable error exists due to impurity of the original salt.

Results.—The readings were generally taken in sets of ten, the potential fall along the tube and the standard resistance being taken in alternate order to compensate for slight changes in the main current. After reversal of the current, another set of ten pairs of readings was taken. The current was then broken and the apparatus left for a few hours before repeating the observations. The whole was then cleaned out, dried, and refilled with fresh solution.

Of 100 results thus obtained for the specific conductivity of *N*-potassium chloride, 20 gave the value 0·1126 mho., 29 gave the value 0·1125 mho., and 51 gave 0·1124 mho. at 25°.

The average value is therefore 0·11247 mho., which is higher than that given by Kohlrausch by 0·6 per cent. Since the current used by Kohlrausch was obtained from a small induction coil, which does not give a symmetrical alternating current, polarisation effects were probably present, and his result is probably too low. It is

unlikely that the error in the present work exceeds 0·1 per cent., and 0·1125 is therefore nearer the true value than 0·1118.

Sodium Chloride Saturated at 25°.—Similar precautions were taken to secure purity of materials as in the case of potassium chloride.

The solution was made by shaking excess of the pure salt with conductivity water at 60° for fifteen minutes, and allowing to remain with occasional shaking for twenty-four hours in a thermostat at 25°. Calomel electrodes were used as before.

The final value obtained was 0·2520(5), which is greater than that given by Kohlrausch by 0·3 per cent.

N-*Silver Nitrate* (169·89 *grams per litre at* 18°).—The main electrodes in this case were plates of pure assay silver, "1000 quality." Secondary electrodes of the same material were tried, but were not so satisfactory as calomel electrodes with a connecting liquid of *N*-potassium nitrate.

The value obtained for the specific conductivity was 0·07796 mho. at 25°.

The value calculated from that of Kohlrausch and Steinwehr (*Sitzungsber. K. Akad. Wiss. Berlin*, 1902, 587) by means of the temperature coefficients given by Déguisne (*Diss.*, Strassburg, 1895) is 0·0779 mho. at 25°.

N-*Sulphuric Acid* (49·043 *grams per litre at* 18°).—The purest available materials were used, and the acid was estimated gravimetrically by precipitation with barium chloride and volumetrically by titration with sodium carbonate.

Mercurous sulphate electrodes were used for both primary and secondary electrodes, and were found to be satisfactory only if used within twenty-four hours of making up. After this time, the mercurous salt gradually dissolves in the acid, increasing its conductivity by 0·1 per cent. in three days, and still more on longer keeping. This raises doubts as to the trustworthiness of the mercurous sulphate electrode for prolonged investigations. No change could be detected within the first twenty-four hours.

The value obtained for the specific conductivity was 0·2137 mho. at 25°.

Kohlrausch gives the value 0·1980 mho. and Loomis (*Ann. Phys. Chem.*, 1897, [iii], **60**, 547) gives 0·195 mho., both at 18°. Using Gotrian's data for temperature coefficient (*Ann. Phys. Chem.*, 1874, [ii], **151**, 378), these give the values 0·2220 and 0·2186 respectively at 25°, which exceed the value found here by 3·6 and 2·2 per cent. respectively.

Summary.

A form of conductivity apparatus is described in which direct current is used and disturbing effects of polarisation at the electrodes are eliminated.

The following values have been obtained for the specific conductivity of solutions in mhos. at 25°:

N-Potassium chloride (74·59 grams per litre at 18°), 0·1124(7).
Sodium chloride saturated at 25°, 0·2520(5).
N-Silver nitrate (169·89 grams per litre at 18°), 0·07796.
N-Sulphuric acid (49·043 grams per litre at 18°), 0·2137.

In conclusion, the author wishes to thank Prof. A. Lapworth for his interest in this work.

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LXII.—*The Abnormality of Strong Electrolytes. Part III. The Osmotic Pressure of Salt Solutions and Equilibrium between Electrolytes.*

By JNANENDRA CHANDRA GHOSH.

IN the previous papers (this vol., pp. 449, 627) it has been shown that the number of free ions in a given solution containing a gram-molecule of salt is

$$n.N.e^{-\frac{A}{nRT}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where N is Avogadro's number, n is the number of ions into which a molecule dissociates, and A is the work required to separate the component ions of a gram-molecule to an infinite distance apart at that particular dilution. It has also been established that only these free ions take part in the conduction of electricity through solutions.

An equation of state free from any arbitrary assumption was deduced by Clausius (*Phil. Mag.*, 1870, [iv], **40**, 122; Jeans, "Dynamical Theory of Gases," 2nd edition, pp. 141—145) from purely dynamical principles, which takes into account the forces of molecular attraction. His theorem $PV=\frac{2}{3}$ kinetic energy $-\frac{1}{3}$ virial is specially suitable for application to salt solutions, since

the work necessary to overcome the forces of electrical attraction in this case can be easily calculated. Milner (*Phil. Mag.*, 1912, [vi], **23**, 551; 1913, **25**, 747) has already developed a method for calculating the virial of solutions of univalent binary electrolytes, and has shown that the Clausius theorem agrees well with experimental results. No relation between the activity coefficient $\frac{\mu_v}{\mu_\infty}$ and the osmotic pressure of salt solutions has, however, yet been established on the basis of complete ionisation at all dilutions. We have seen that the molecular conductivity is proportional to the number of free ions, $n.N.e^{-\frac{A}{nRT}}$. Since at infinite dilution $A=0$,

$$\frac{\mu_v}{\mu_\infty} = e^{-\frac{A}{nRT}},$$

or

$$A = nRT \log_e \frac{\mu_\infty}{\mu_v} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

which holds good for all types of salt solutions. Here A, of course, is the virial, and PV thus becomes equal to

$$nRT - \tfrac{1}{3}nRT \log_e \frac{\mu_\infty}{\mu_v},$$

$$= nRT\left\{1 - \tfrac{1}{3}\log_e \frac{1}{a}\right\},$$

or

$$i = n.\left\{1 - \tfrac{1}{3}\log_e \frac{1}{a}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

According to Arrhenius, on the view that in a solution we have an equilibrium between ions and undissociated molecules,

$$i = 1 + (n-1)a \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

At infinite dilution, equations (3) and (4) lead to the same limiting value of $i=n$. At other dilutions, the two equations give different results. In this paper it is proposed to examine which of these equations agrees best with actual observations.

Determination of a for Univalent Binary Electrolytes at Various Dilutions.

It has already been shown that the variation of activity-coefficient with dilution for univalent binary electrolytes is given by the equation

$$\frac{N.E^2.\sqrt[3]{2N}}{D.\sqrt[3]{V}} = 2RT \log_e \frac{\mu_\infty}{\mu_v} = 2RT \log_e \frac{1}{a}.$$

The agreement with the observed values is quite satisfactory for dilutions of 10 litres and upwards (Part I). This coincidence becomes, however, less perfect as the concentration increases. This is certainly due to the fact, suggested by Washburn (*J. Amer. Chem. Soc.*, 1911, **33**, 1464), and later emphasised by Noyes and Falk (*ibid.*, 1912, **34**, 458), that the ratio $\frac{\mu_v}{\mu_\infty}$ is not a true measure of the activity-coefficient. A correction for change in ionic mobility, due to the change in the viscosity of solutions with dilution, is necessary; the ratio $\frac{\mu_v\eta_v}{\mu_\infty\,\eta_\infty}$, furnishes a much closer approximation to the true values of the activity-coefficient than the ratio $\frac{\mu_v}{\mu_\infty}$. Taking into account this correction for viscosity, the equation for univalent binary electrolytes becomes

$$A = \frac{N.E^2.\sqrt[3]{2N}}{D.\sqrt[3]{V}} = 2RT\log_e\frac{\mu_\infty\,\eta_\infty}{\mu_v\eta_v} = 2RT\log_e\frac{1}{a}. \quad . \quad (5)$$

From table I it will be evident that, with this modification, the above equation can be very well applied to concentrations up to $0{\cdot}5N$. In the table, the values of μ_v and η_v have been taken from the paper of Noyes and Falk (*loc. cit.*). The striking regularity brought to notice by these investigators, that salts of analogous constitution have the same activity-coefficient at the same dilution, is, of course, a necessary deduction of the above equation. Above $0{\cdot}5N$, the volume actually occupied by the solute molecules is not negligible.

TABLE I. T=18°.

Salt.	Extrapolation value of $\mu_\infty\eta_\infty$.	Calc. value of $\mu_\infty\eta_\infty$ from $\mu_{10}\eta_{10}$.		$v=$ 2.	5.	10.	20.
1. NaCl	108·9	109·8	$\mu_v\eta_v$ calc.	82·3	88·8	92·7	96·1
			$\mu_v\eta_v$ obs.	84·2	89·1	92·7	96·1
2. KCl	130·0	132·5	$\mu_v\eta_v$ calc.	99·2	107·0	111·8	115·8
			$\mu_v\eta_v$ obs.	101·3	107·5	111·8	115·6
3. LiCl	98·8	99·0	$\mu_v\eta_v$ calc.	74·2	80·0	83·6	86·7
			$\mu_v\eta_v$ obs.	75·5	80·2	83·6	86·6
4. KBr	132·2	134·5	$\mu_v\eta_v$ calc.	101·0	108·6	113·5	117·6
			$\mu_v\eta_v$ obs.	101·3	109·1	113·5	117·4
5. KI	131·2	133·8	$\mu_v\eta_v$ calc.	100·1	—	112·9	116·9
			$\mu_v\eta_v$ obs.	101·4	—	112·9	116·7

It will be observed that the difference between the calculated value of μ_∞ and the extrapolation value, obtained by means of empirical equations, is within 2 per cent.

TABLE II.

	$V=2.$	5.	10.	20.	50.	100.
Theoretical value of α for all univalent binary electrolytes according to equation 5. Per cent.....	74·8	80·8	84·4	87·5	90·6	92·4

Variation of α with Dilution for Ternary Electrolytes.

For ternary electrolytes, the variation of activity-coefficient with dilution is very satisfactorily represented by the equation

$$\frac{6N \cdot E^2 \cdot \sqrt[3]{2N}}{D \cdot \sqrt{3} \cdot \sqrt[3]{V}} = 3RT \log_e \frac{\mu_\infty}{\mu_v} = 3RT \log_e \frac{1}{\alpha}.$$

In table III, the percentage values of α, calculated from the above equation for various dilutions, are given.

TABLE III.

$v=$	10.	20.	40.	50.	100
$\alpha=$	67·8	73·5	78·3	79·7	84·0

Determination of the Value of i for Univalent Binary Electrolytes.

The method of determining i with sufficient exactness is based on observations on the lowering of the freezing point of salt solutions. Attempts were made to determine i from the diminution of the vapour pressure of solutions (compare Menzies, *Zeitsch. physikal. Chem.*, 1911, **76**, 231), but until the recent work of Lovelace, Frazer, and Miller (*J. Amer. Chem. Soc.*, 1916, **38**, 515) the methods were not sufficiently accurate. These investigators have succeeded in improving the technique of the method to such an extent that the temperature of the bath can be kept constant within 0·001° for more than twelve hours, and a pressure of 0·0001 mm. can be exactly measured. The results obtained by them are rather peculiar, inasmuch as the molecular lowering of the vapour pressure of a solution of potassium chloride remains constant as the concentration changes from $2N$ to $0{\cdot}2N$. Any opinion on these results must at present be suspended, as the work is still in progress.

The method based on the lowering of the freezing point has been well investigated, and all the observations, with the exception of those of Ponsot (*Ann. Chim. Phys.*, 1897, [vii], **10**, 79; 1899, **16**, 162), go to show that i continually increases until the limiting

value n is reached. Noyes and Falk, in their valuable paper on the properties of salt solutions (*J. Amer. Chem. Soc.*, 1910, **32**, 1020), have given a fairly complete account of the investigations on the lowering of the freezing point up to that time. They have not attached the same weight to the data obtained by different investigators, and hence their mean value of i is somewhat arbitrary. In table IV I have recalculated the mean value of the molecular lowering of the freezing point on the simpler, but still arbitrary, basis that the probable error of the various investigators is approximately the same. The value of i is obtained by dividing the mean molecular lowering of the freezing point by 1·858. In the footnote are given the references to the work of the investigators whose data have been utilised in calculating the mean value of i.

The weighted mean of the "molecular number i" for salts of the uni-univalent type, obtained by Noyes and Falk (*loc. cit.*, p. 1027), is included in table VIII for the sake of comparison. It should be noted that this mean was obtained by excluding the data on the molecular numbers of lithium chloride and sodium bromide. The values of i for these salts, as will be seen from table IV, are always higher than the mean. For ternary electrolytes, Noyes and Falk do not give any weighted mean, but observe that "the values of the molecular numbers are of similar magnitude, the range being 2·57 to 2·68 at dilution 10 and 2·71 to 2·77 at dilution 50."

TABLE IV.

Salt.	$V=2$.	5.	10.	20.	50.	100.
KCl[1]	1·800	1·833	1·862	1·886	1·922	1·947
NaCl[2]	1·824	1·850	1·880	1·897	1·928	1·945
LiCl[3]	—	—	1·901	1·912	1·928	1·937
CsCl[4]	1·780	—	1·878	1·892	1·930	—
NaBr[5]	—	1·871	1·891	1·911	—	—
KBr[6]	1·813	1·841	1·870	1·910	1·929	—

[1] Jones, *Zeitsch. physikal. Chem.*, 1893, **11**, 110; **12**, 639. Loomis, *Ann. Phys. Chem.*, 1894, [iii], **51**, 500; 1896, **57**, 495; 1897, **60**, 523; *Zeitsch. physikal. Chem.*, 1900, **32**, 578; 1901, **37**, 406. Lewis, *ibid.*, 1894, **15**, 365. Abegg and Nernst, *ibid.*, 1894, **15**, 681; 1896, **20**, 207. Whetham, *ibid.*, 1900, **33**, 344. Raoult, *ibid.*, 1898, **27**, 617. Jahn, *ibid.*, 1905, **50**, 129; 1907, **59**, 31. Richards, *ibid.*, 1903, **44**, 563. Ponsot, *loc. cit.* Bedford, *Proc. Roy. Soc.*, 1910, [*A*], **83**, 454.

[2] Jones, Loomis, Raoult, Ponsot, Abegg, Jahn, Hausrath, *Ann. Physik*, 1902, [iv], **9**, 522. Osaka, *Zeitsch. physikal. Chem.*, 1902, **41**, 560.

[3] Loomis, Jahn.

[4] Jahn, Biltz, *Zeitsch. physikal. Chem.*, 1902, **40**, 185.

[5] Jahn.

[6] Jahn, Biltz.

TABLE V.

Mean value of i for univalent binary electrolytes at various dilutions.

$v=$	2.	5.	10.	20.	50.	100.
$i=$	1·805	1·849	1·880	1·900	1·935	1·942

Determination of i *for Ternary Electrolytes at Various Dilutions.*

In calculating the value of i, the method described before has been followed. Table VI contains the mean value of i for some well-investigated ternary electrolytes at various dilutions.

TABLE VI.

Salt.	Mean value of i.	$v=10.$	20.	50.
$CaCl_2$[1]	i =	2·624	2·685	2·789
$MgCl_2$[2]	i =	2·677	2·708	2·763
$SrCl_2$[3]	i =	2·629	2·673	2·781
$BaCl_2$[4]	i =	2·580	2·640	2·712
$ZnCl_2$[5]	i =	2·579	2·666	2·771
$CO(NO_3)$[6] ...	i =	2·700	2·760	—
$Cu(NO_3)$[7] ...	i =	2·630	2·730	—
$Ni(NO_3)_2$[8] ...	i =	2·600	2·670	2·810

[1] Loomis, Ponsot, Jones and Pearce. [2] Loomis. [3] Loomis, Jones and Pearce. [4] Bedford, Loomis, Jones, Ponsot, Whetham. [5] Jones. [6] Jones and Pearce. [7] Jones and Pearce. [8] Jones and Pearce.

TABLE VII.

Mean value of i for ternary electrolytes at various dilutions.

$v=$	10.	20.	50.
$i=$	2·620	2·691	2·771

The Validity of the Clausius Theorem.

TABLE VIII.

	$v=$ 2.	5.	10.	20.	50.	100.
i According to Noyes and Falk	1·804	1·837	1·865	1·887	1·925	1·937
i Observed for univalent binary salts	1·805	1·849	1·880	1·900	1·935	1·942
i According to equation 3	1·806	1·859	1·887	1·910	1·934	1·947
i According to equation 4	1·748	1·808	1·844	1·875	1·906	1·924

TABLE IX.

	$v=10.$	20.	50.
i Observed for ternary salts	2·620	2·691	2·771
i According to equation 3	2·616	2·695	2·773
i According to equation 4	2·356	2·470	2·594

It is evident that the equation

$$i = n\left\{1 - \tfrac{1}{3}\log_e \frac{\mu_\infty}{\mu_v}\right\},$$

based on the Clausius theorem, agrees best with the experimental results. The Arrhenius equation fails conspicuously in the case of ternary electrolytes. Jones attempted to explain this anomaly by his hydrate theory. The high value of i according to him, is due to the fact that the solvent combines with the solute, the ratio of solute to solvent molecules increases, and hence i becomes abnormally large. His theory may be correct for concentrated solutions. There is, however, some inherent improbability in the fact that in dilute solutions about 150 water molecules must be made to combine with an ion in order that the difference between the observed value of i and that calculated from Arrhenius's equation may be explained. The hydrate theory of dilute solutions becomes simply unnecessary in view of the complete validity of the Clausius theorem as applied to salt solutions.

Activity-coefficient of Salts in Mixed Solutions.

Here we have the following empirical rule: "The conductivity and the freezing-point lowering of a mixture of salts having one ion in common are those calculated under the assumption that the degree of ionisation (activity-coefficient) of each salt is that which it would have if it were present alone at such an equivalent concentration, that the concentration of either of its ions is equal to the sum of the equivalent concentrations of all the positive or negative ions present in the mixture" (A. A. Noyes, *Tech. Quart.*, 1904, **17**, 301).

Let there be two solutions of sodium chloride and potassium chloride, and let their equivalent dilutions be V and V' respectively. If X and Y are their respective activity-coefficients, then

$$\log \frac{1}{x} = k\left(\frac{1}{V}\right)^{\frac{1}{3}},$$

and

$$\log \frac{1}{y} = k\left(\frac{1}{V'}\right)^{\frac{1}{3}}.$$

If the two solutions are mixed together, the total volume $= V + V'$. But, on mixing, there is a distribution of arrangement until the entire solution is uniform. Since there are only ions in a solution, and since the arrangement in sodium chloride and potassium chloride solutions is identical, the distance between the sodium and chlorine ions in an electric doublet is the same as it would have

been if the dilution were $\frac{V+V'}{1+1}$. The result is that the activity-coefficient of sodium chloride in the mixture corresponds with that of the pure solution at dilution $\frac{V+V'}{2}$, which is the equivalent dilution of the common ion. The same is true for potassium chloride. On mixing, therefore,

$$\log \frac{1}{x'} = k\left(\frac{2}{V+V'}\right)^{\frac{1}{3}},$$

$$\log \frac{1}{y'} = k\left(\frac{2}{V+V'}\right)^{\frac{1}{3}}.$$

where x' and y' are the respective activity-coefficients of the salts in the mixture.

Therefore $X'=Y'$, or the activity-coefficient of each of the salts is the same and corresponds with that of a solution the equivalent concentration of which is equal to the sum of the equivalent concentrations of all the positive or negative ions present in the mixture.

If $V=V'$, that is, if the initial concentration of both solutions is the same,

$$\frac{1}{V} = \frac{1}{V'} = \frac{1+1}{V+V'},$$

therefore $X=Y=X'=Y'$. That is, the activity-coefficient does not change when two salt solutions having the same equivalent concentration are mixed. This is the condition for isohydry.

Conclusions.

In this series of papers on the abnormality of strong electrolytes, I have proceeded on the following assumptions:

(1) A salt solution is always completely ionised, the force of attraction between ions being governed by the law of inverse squares.

(2) The arrangement of ions in a univalent binary electrolyte corresponds with a simple cubic lattice, whilst in a solution of a ternary electrolyte the arrangement corresponds with a fluorspar lattice.

The following equations have been derived:

I. $A = \frac{N.E^2.\sqrt[3]{2N}}{D.\sqrt{V}} = 2RT\log_e\frac{\mu_\infty}{\mu_v}$ . . . for universal binary salts.

II. $A = \frac{6N.E^2.\sqrt[3]{2N}}{D.\sqrt{3}.\sqrt[3]{V}} = 3RT\log_e\frac{\mu_\infty}{\mu_v}$ . . . for ternary salts.

III. $i = n\left\{1 - \frac{1}{3}\log_e\frac{\mu_\infty}{\mu_v}\right\}$

The validity of these fundamental equations has been completely demonstrated both in aqueous and non-aqueous solutions. The variation of the activity-coefficient with temperature has been successfully calculated, and the conditions for isohydry have been determined. In fact, a complete theory of dilute salt solutions has been propounded.

My best thanks are due to Prof. P. C. Rây and to my friend and colleague Mr. J. N. Mukherjee, M.Sc.

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LXIII.—*The Preparation of certain Organic Stanno- and Stanni-chlorides.*

By JOHN GERALD FREDERICK DRUCE.

DOUBLE haloids of tin with organic bases have long been known. Thus Cook (*Amer. Chem. J.*, 1899, **22**, 435) described a number of aliphatic amine salts, and Slagle (*ibid.*, 1898, **20**, 633) prepared the aniline and toluidine compounds. Pyridine stannochloride has been described by Hayes (*J. Amer. Chem. Soc.*, 1902, **24**, 360), and pyridine stannichloride by Weinland and Bames (*Zeitsch. anorg. Chem.*, 1909, **62**, 250). The quinoline salts have been isolated by Borsbach (*Ber.*, 1890, **23**, 431).

These salts were usually prepared from hydrochloric acid solutions of the component haloids, and the same method of preparation has been employed in the case of the new compounds described below.

EXPERIMENTAL.

Diethylamine Stannochloride, $(NHEt_2)_2,H_2SnCl_4$.—This salt was isolated from a dilute hydrochloric acid solution containing two molecular proportions of amine to one of stannous chloride. The crystals which separated were collected and dried on a porous plate in a desiccator over sodium hydroxide. The salt was very deliquescent and melted at 58°:

0·9852 gave 0·3640 SnO_2. Sn = 29·11.
0·5950 „ 0·8355 AgCl. Cl = 34·75.
$(C_4H_{11}N)_2,H_2SnCl_4$ requires Sn = 29·04; Cl = 34·69 per cent.

o-Toluidine Stannochloride, $(C_7H_7\cdot NH_2)_2,H_2SnCl_4$.—*o*-Toluidine (5·35 grams) was added to 100 c.c. of a dilute hydrochloric acid solution containing 5·65 grams of stannous chloride, and warmed. On cooling, fine, silky needles, melting at 164°, were deposited.

The salt dissolved readily in cold water, the solution remaining clear unless boiled:

0·4385 gave 0·1382 SnO_2. Sn = 24·82.
0·1205 „ 0·1454 AgCl. Cl = 29·85.
$(C_7H_9N)_2,H_2SnCl_4$ requires Sn = 24·90; Cl = 29·75 per cent.

o-Toluidine Stannichloride, $(C_7H_9N)_2,H_2SnCl_6,H_2O$.—This compound was obtained in very pale pink, short needles, which began to decompose at 210°:

0·8247 gave 0·2274 SnO_2. Sn = 21·23.
0·1228 „ 0·1841 AgCl. Cl = 37·39.
$(C_7H_9N)_2,H_2SnCl_6,H_2O$ requires Sn = 21·01; Cl = 37·64 per cent.

Methylaniline Stannochloride, $C_7H_9N,HSnCl_3$.—Redistilled methylaniline (5·35 grams) and stannous chloride (5·65 grams) were dissolved together in 100 c.c. of hot dilute hydrochloric acid. The clear solution deposited a mass of short, stout, colourless prisms dissolving in water to a clear solution, which became turbid only on boiling. The salt is also soluble in alcohol, but not in chloroform, and melts at 106°:

0·2549 gave 0·1157 SnO_2. Sn = 35·75.
0·3264 „ 0·4224 AgCl. Cl = 32·02.
$C_7H_9N,HSnCl_3$ requires Sn = 35·63; Cl = 31·93 per cent.

Methylaniline Stannichloride, $(C_7H_9N)_2,H_2SnCl_6$.—Molecular proportions of the base and hydrated crystalline stannic chloride were dissolved together in dilute hydrochloric acid. Colourless crystals of the stannichloride, melting and decomposing at 251°, separated from the solution. The salt dissolved in water to a clear solution, which was not appreciably hydrolysed even when boiled:

0·5054 gave 0·1401 SnO_2. Sn = 21·78.
0·1728 „ 0·2703 AgCl. Cl = 38·71.
$(C_7H_9N)_2,H_2SnCl_6$ requires Sn = 21·67; Cl = 38·84 per cent.

Chlorination of a dilute hydrochloric acid solution of the stannochloride also gave this compound, but the product was not pure and had a low melting point.

m-Phenylenediamine Stannochloride, $C_6H_4(NH_2)_2,2HSnCl_3$.—This compound was obtained by reducing *m*-nitroaniline or *m*-dinitrobenzene with tin and hydrochloric acid. It forms fine, silky prisms, melting at 128°, which are soluble in water, but the

solution soon becomes cloudy. Dilute hydrochloric acid solutions of the salt gave the reactions for stannochlorides, for example, iodine solutions were decolorised; a white precipitate was obtained with mercuric chloride solution, which darkened on warming, and a dark brown precipitate of stannous sulphide was obtained by passing in hydrogen sulphide:

0·4211 gave 0·2232 SnO_2. Sn = 41·75.
0·4537 „ 0·6891 AgCl. Cl = 37·58.
$C_6H_8N_2,2HSnCl_3$ requires Sn = 41·85; Cl = 37·97 per cent.

m-*Phenylenediamine Stannichloride*, $C_6H_8N_2,H_2SnCl_6$.—Dilute hydrochloric acid solutions of the above stannochloride were oxidised to stannochloride on exposure to air, but the crystals isolated from these solutions were not pure. The pure salt was obtained from *m*-nitroaniline (2·56 grams) or from *m*-dinitrobenzene (1·3 grams) and stannous chloride (10·5 grams). Almost colourless crystals of the stannichloride separated from the hydrochloric acid solution. It dissolved readily in cold water, and the solution did not hydrolyse unless heated. The crystals melted and decomposed at 265°:

0·4762 gave 0·1606 SnO_2. Sn = 26·56.
0·4511 „ 0·8767 AgCl. Cl = 48·07.
$C_6H_8N_2,H_2SnCl_6$ requires Sn = 26·88; Cl = 48·18 per cent.

No double haloids of *o*-phenylenediamine could be prepared.

p-*Phenylenediamine Stannochloride*, $C_6H_8N_2,H_2SnCl_4$. —This salt was obtained as a mass of compact, opaque, white crystals readily soluble in water. The solution was easily hydrolysed by gently warming. The crystals melted and decomposed at 270°:

0·5547 gave 0·2246 SnO_2. Sn = 31·90.
0·5547 „ 0·8436 AgCl. Cl = 37·63.
$C_6H_8N_2,H_2SnCl_4$ requires Sn = 32·06; Cl = 38·26 per cent.

p-*Phenylenediamine Stannichloride*, $C_6H_8N_2,H_2SnCl_6$.—Oxidation of solutions of the stannochloride gave impure stannichloride. A pure specimen was obtained by treating *p*-nitroaniline with a molecular proportion of stannous chloride in hydrochloric acid. The nacreous plates dissolved in cold water without appreciable hydrolysis, but, on boiling, a precipitate was formed. The salt melted and decomposed at 230°:

0·3784 gave 0·1282 SnO_2. Sn = 26·69.
0·1180 „ 0·2305 AgCl. Cl = 48·32.
$C_6H_8N_2,H_2SnCl_6$ requires Sn = 26·88; Cl = 48·18 per cent.

Benzylamine Stannochloride, $C_6H_5\cdot CH_2\cdot NH_2,HSnCl_3$.—This salt was obtained by warming together benzonitrile (5 grams) and tin

(12 grams) in 50 c.c. of concentrated hydrochloric acid diluted with 20 c.c. of water under a reflux condenser for three hours. On cooling, a mass of short, silky crystals was deposited, which gave the usual reactions for stannochlorides, and softened at 95° and decomposed at about 210°:

0·4491 gave 0·2045 SnO_2. Sn = 35·70.
0·2864 „ 0·3592 AgCl. Cl = 31·03.
$C_7H_9N,HSnCl_3$ requires Sn = 35·63; Cl = 31·93 per cent.

Benzylamine Stannichloride, $(C_7H_9N)_2,H_2SnCl_6$.—Benzonitrile (2·06 grams) was heated with stannous chloride (9·04 grams) in hydrochloric acid, with shaking, under a reflux condenser until a clear solution was obtained. From this, soft, shining crystals separated in flakes resembling naphthalene and melting at 112°:

0·3465 gave 0·0943 SnO_2. Sn = 21·51.
0·3465 „ 0·5421 AgCl. Cl = 38·83.
$(C_7H_9N)_2,H_2SnCl_6$ requires Sn = 21·85; Cl = 38·84 per cent.

p-*Methylbenzylamine Stannochloride*,
$CH_3{\cdot}C_6H_4{\cdot}CH_2{\cdot}NH_2,HSnCl_3$.
—Ten grams of tin and 5 grams of *p*-toluonitrile were heated with hydrochloric acid as in the case of the benzylamine salt, which this compound also resembled in properties. Both dissolved slowly in water, and the solutions soon decomposed. On heating, it melted at 107°:

0·5248 gave 0·2290 SnO_2. Sn = 34·38.
$C_8H_{11}N,HSnCl_3$ requires Sn = 34·29 per cent.

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LXIV.—*The Basic Carbonates of Copper.*

By HORACE BARRATT DUNNICLIFF and SUDARSHAN LAL.

IN connexion with an investigation of the composition of a cellulose cuprammonium–hydroxide solution made by dissolving cotton-wool in a solution of commercial copper carbonate in ammonium hydroxide, one of the authors had occasion to examine a number of samples of commercial "copper carbonate."

Pickering (T., 1909, **95**, 1410) states that the ordinary copper carbonate of commerce has the formula $2CuO,CO_2,H_2O$, identical

with malachite. The present paper does not support that statement.

According to some text-books, also, the compound precipitated when sodium carbonate is added to a solution of copper carbonate in the cold has the composition $2CuO,CO_2,2H_2O$, which changes to $2CuO,CO_2,H_2O$ on keeping.

The amount of copper oxide in thirteen different samples of commercial copper carbonate from different European and Indian sources is shown in table I. The percentages of copper oxide theoretically found in the basic carbonates of copper, for which a definite composition is claimed, are also quoted for purposes of comparison and reference.

TABLE I.

Percentage of Copper Oxide found in Thirteen Samples of Commercial Copper Carbonate.

1	2	3	4	5	6	7	8	9	10	11	12	13
78·60	71·71	71·52	69·69	69·58	69·55	69·29	68·90	68·61	68·41	68·36	67·84	66·16

Small quantities of impurity were present, usually iron, but in no case was the amount sufficient to account for the widely different results.

Name of Compound.	CuO per cent.	CO_2 per cent.	H_2O per cent.
Pickering's compound (*loc. cit.*), $8CuO,3CO_2,6H_2O$	72·62	15·06	12·32
Malachite, $CuCO_3,Cu(OH)_2$ or $2CuO,CO_2,H_2O$	71·94	19·95	8·11
Azurite, $2CuCO_3,Cu(OH)_2$ or $3CuO,2CO_2,H_2O$	69·23	25·54	5·22
$CuCO_3,Cu(OH)_2,H_2O$ or $2CuO,CO_2,2H_2O$	66·53	18·41	15·06

Assuming that the commercial copper carbonates have the composition of malachite, it was thought that the adsorption of moisture on exposure to the atmosphere might account for the low results found. In order to test this, copper carbonate, in the form of a fine powder and spread in thin layers, was first dried in a steam-oven at 97° for more than three hours, and then, after weighing, was exposed to the atmosphere of the laboratory for three days (15—17°) and weighed at intervals. The amount of increase in weight fluctuated during this time, but the maximum increase recorded amounted to 1·06 per cent. This would not account for the variations in copper oxide content shown in table I.

If the copper oxide content is any indication of the composition of the compound, it would appear that the commercial compound more nearly approximates to the composition of azurite. In order to obtain further evidence on this point, five samples were examined

which contained from 69·55 to 71·71 per cent. of copper oxide. The same samples contained from 17·35 to 18·1 per cent. of carbon dioxide. Comparison with the above table will show that these results are much below those required for malachite or azurite. It appears from this that the statement that commercial copper carbonate has the same composition as malachite is incorrect, and that in reality the substance is a mixture of very varying composition.

The authors of the present paper made various attempts to prepare a basic carbonate of copper of approximately constant composition in a simple manner, as it was desired to devise a process which could be used by comparatively inexperienced workers. Table II shows the methods employed and the percentages of copper oxide obtained.

TABLE II.

Method.	CuO per cent.
Copper sulphate solution precipitated in the cold with cold sodium carbonate solution	71·82
Copper sulphate solution (hot) precipitated with cold sodium carbonate solution	78·85
Copper sulphate solution (cold) precipitated with cold saturated solution of sodium hydrogen carbonate	77·09
Copper sulphate solution (cold) precipitated with cold 5 per cent. sodium hydrogen carbonate solution	71·08
Boiling saturated copper sulphate solution precipitated with cold saturated sodium hydrogen carbonate solution. The burner was removed before the addition of the sodium hydrogen carbonate	72·37

In all cases, the precipitates were washed free from sulphate.

These results yielded no valuable prospects, and it was decided to see if the desired result could be achieved by taking solutions of known strength. In the earlier experiments (from which tables I and II are compiled), the carbonates were carefully heated in a crucible, the residue being cooled in a desiccator and weighed. The heating, etc., was repeated until a constant weight was obtained. This method presents several defects, and it was decided to make complete analyses of the substances produced. This was done by heating a weighed amount of the substance in a boat contained in a short, lead-glass tube, the water and carbon dioxide being collected by means of the usual absorption apparatus employed in organic combustions. All heating was done by means of Bunsen burners manipulated by hand, and the experiment was carried out in an atmosphere of dry oxygen.

It was observed that in one or two cases the copper oxide was distinctly crystalline in appearance. In all the other cases, the

copper oxide was very dark brown, not black. Tests performed on the oxide showed it to be free from impurity.

A saturated solution of purified copper sulphate (14·5°) was diluted with an equal volume of distilled water, and to the cold solution was added a cold (14·5°) solution of pure sodium carbonate (10 per cent.). The precipitate was allowed to remain for twenty-four hours, and then washed on a Büchner funnel with distilled water until free from sulphate. The precipitate, on solution, contained no sulphate. It was dried in a steam-oven at 96° until its weight was constant.

TABLE III.

	CuO per cent.	CO_2 per cent.	H_2O per cent.	Total per cent.
The average composition of the precipitate was	72·98	15·46	11·89	100·33
$13CuO,5CO_2,9H_2O$ requires	73·02	15·54	11·44	100·00
Pickering's compound $8CuO,3CO_2,6H_2O$ requires	72·62	15·06	12·32	100·00

The above percentages give the formula: $13·07CuO,5CO_2,9·40H_2O$.

The Basic Carbonate, $2CuCO_3,5Cu(OH)_2$ *or* $7CuO,2CO_2,5H_2O$.

A solution of pure copper sulphate, saturated at 14·5°, was diluted with an equal quantity of distilled water, and to this solution was added a solution containing 5 per cent. of sodium carbonate and 5 per cent. of sodium hydrogen carbonate. The carbonate solution was added with stirring until, on filtering a small portion, the filtrate gave no precipitate with it. The mixture was allowed to remain until next day, and was then filtered on a Büchner funnel and washed free from sulphate. This required

TABLE IV.

No.	CuO per cent.	CO_2 per. cent.	H_2O per cent.	Total per cent.
(*a*) Mean of three analyses	75·90	11·25	12·78	99·93
(*b*) Mean of four analyses	75·48	11·55	13·18	100·21
(*c*) Mean of three analyses	75·39	12·04	12·88	100·31
Mean	75·59	11·61	12·95	100·15
$2CuCO_3,5Cu(OH)_2$ requires	75·77	11·98	12·25	100·00

Stated as formulæ the above results become:—

(*a*) $7CuO,1·89CO_2,5·20H_2O$.
(*b*) $7CuO,1·93CO_2,5·39H_2O$.
(*c*) $7CuO,2·01CO_2,5·28H_2O$.
Mean: $7CuO,1·94CO_2,5·29H_2O$.
Theory: $7CuO,2·00CO_2,5·00H_2O$.

many hours, and usually extended until the next morning. The wet precipitate was then allowed to remain until the third day and dried in a steam-oven. The drying process never lasted less than six hours.

Three separate preparations, (*a*), (*b*), and (*c*), were made. The analyses of these preparations are shown in table IV (p. 721).

Summary.

Examination of a number of samples of commercial copper carbonate gave evidence to show that the statement that it has the same composition as malachite is erroneous.

An attempt has been made to prepare a basic copper carbonate of approximately constant composition from pure materials.

A new basic copper carbonate, $2CuCO_3,5Cu(OH)_2$ or

$$7CuO,2CO_2,5H_2O,$$

is described.

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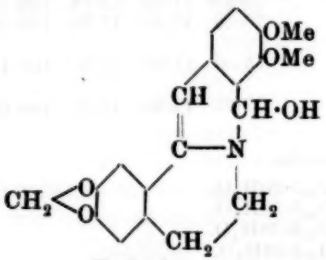
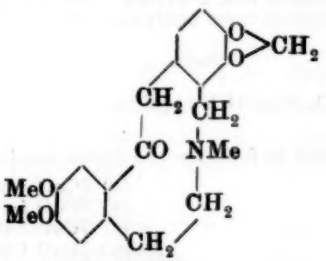
LXV.—*A Study of some Derivatives of Berberine Closely Allied to Derivatives of Cryptopine.*

By WILLIAM HENRY PERKIN, jun.

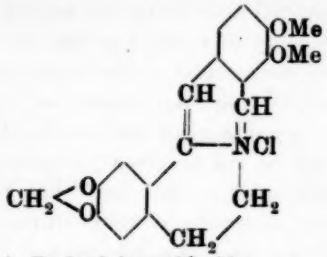
THE close relationship which exists between berberine and cryptopine has been discussed on more than one occasion (compare T., 1916, **109**, 833, 841; this vol., p. 493), and it has been pointed out that, if the formulæ of the alkaloids, or better still of their quaternary salts, are written side by side, it is readily seen that the difference between the two is, in the main, the presence of the *N*-methyl group in cryptopine and its absence in the berberine



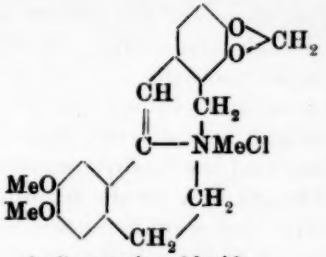
Berberine.



Cryptopine.

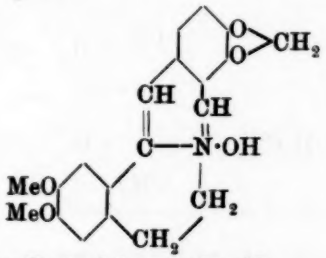


Berberinium chloride.



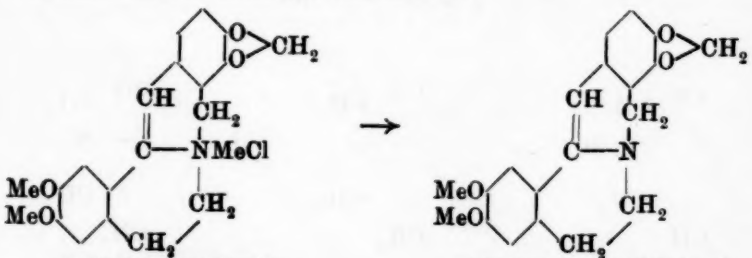
*iso*Cryptopine chloride.

molecule, and the fact that the positions of the two methoxy-groups and the methylenedioxy-group are reversed in the two formulæ. It was further pointed out that the alkaloid of the berberine type which actually corresponds with cryptopine is *epi*berberinium hydroxide,



*epi*Berberinium hydroxide.

and the conversion of cryptopine into this interesting alkaloid has recently been described (this vol., p. 493). The problem which had to be solved in attempting the preparation of *epi*berberine from cryptopine was essentially the discovery of some method which would render possible the removal of the *N*-methyl group from the latter alkaloid, and this difficult step was ultimately accomplished by heating *iso*cryptopine chloride at 280°, when methyl chloride was eliminated according to the scheme:

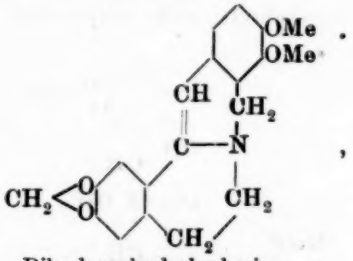


*iso*Cryptopine chloride. Dihydroanhydro*epi*berberine.

The dihydroanhydro*epi*berberine obtained in this way served as the principal source from which a considerable number of derivatives of *epi*berberine were subsequently obtained and examined.

The object of the present investigation was to accomplish the reverse change, namely, to introduce an *N*-methyl group into the berberine molecule in order to study derivatives of berberine which were similarly constituted to corresponding derivatives of cryptopine, and only differed from these in containing the two methoxy-groups and the methylenedioxy-group in the reversed positions. It was hoped that results might be obtained in this way that would confirm and amplify certain curious observations made during the study of the derivatives of cryptopine, and this has proved to be the case.

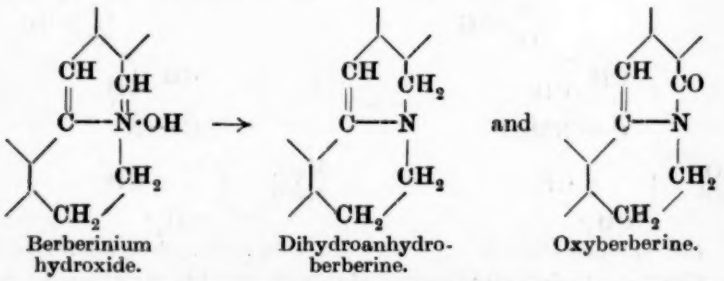
The substance most largely employed for the purposes of this investigation has been dihydroanhydroberberine,*



Dihydroanhydroberberine.

and the opportunity was taken to bring forward additional evidence in support of the identity and constitution of this important substance.

Dihydroanhydroberberine was first obtained by Gadamer (*Arch. Pharm.*, 1905, **243**, 35) during the course of a valuable investigation into the action of alkalis on berberinium hydroxide. Gadamer showed that berberinium sulphate or hydroxide, when heated on the steam-bath with concentrated sodium hydroxide solution, undergoes simultaneous reduction and oxidation with the formation of dihydroanhydroberberine and oxyberberine:



Berberinium hydroxide. Dihydroanhydroberberine. Oxyberberine.

* With regard to the nomenclature employed in this communication for berberine and its derivatives, compare this vol., p. 503.

According to Gadamer, dihydroanhydroberberine melts at 165—167°, crystallises in deep yellowish-brown tablets, yields a hydrochloride, $C_{20}H_{19}O_4N,HCl,3H_2O$, and is readily oxidised on exposure to the air to berberine. At a later date (*Monatsh.*, 1910, **31**, 557), Faltis expressed the opinion that the reaction between berberinium hydroxide and sodium hydroxide was not analogous to the Cannizzaro reaction between aromatic aldehydes and alkali, but was similar to the change which Decker (*Ber.*, 1903, **36**, 2568) has observed to take place when quinoline methiodide is treated with an alkali:

$$3C_9H_7N,MeI + 3NaOH = 2C_9H_6ONMe + C_9H_{10}NMe + 3NaI + H_2O.$$

N-Methylquinolone. *N*-Methyltetrahydroquinoline.

In other words, Faltis was of opinion that the substance which Gadamer had described as dihydro(anhydro)berberine was in reality tetrahydro(anhydro)berberine. That such a suggestion could have been made is remarkable, for, with the exception of almost identical melting points (168—170°), there are scarcely any points of resemblance between dihydroanhydroberberine and tetrahydroanhydroberberine. Tetrahydroanhydroberberine is colourless and gives colourless salts, of which the hydrochloride has the composition $C_{20}H_{21}O_4N,HCl$; dihydroanhydroberberine has a striking, yellowish-brown colour and yields a deep yellow hydrochloride, $C_{20}H_{19}O_4N,HCl,3H_2O$. The mistaken view which Faltis advanced is doubtless partly due to the fact that he used impure dihydroanhydroberberine for his experiments, for he states (*loc. cit.*, p. 567) that the material that he employed melted at 135—155°, whereas pure dihydroanhydroberberine melts at 166—168°.

Faltis further makes the erroneous statement that there is no depression in melting point when equal quantities of dihydroanhydroberberine and tetrahydroanhydroberberine are mixed, whereas the present author finds that such a mixture of the pure substances softens at 140—145°, and is completely melted at 152°. Faltis did not make any comparative analyses of dihydroanhydroberberine and tetrahydroanhydroberberine, or he would have suspected that these substances could not be identical, since the former, $C_{20}H_{19}O_4N$, contains C = 71·2, H = 5·6, whereas the latter, $C_{20}H_{21}O_4N$, contains C = 70·8, H = 6·2, a difference quite easily detected by accurate analysis (compare p. 739). The only positive evidence which Faltis brings forward in support of his view that these bases are identical is that they require approximately equal amounts of iodine to oxidise them to berberine. A method of this kind carried out under the conditions observed by Faltis would be

open to grave suspicion in any case, and is obviously quite valueless when impure material is employed in the determinations.

The contention that dihydroanhydroberberine and tetrahydroanhydroberberine are identical was subsequently dealt with by Gadamer (*Arch. Pharm.*, 1910, **248**, 670), who not only discussed in detail the points raised by Faltis and showed that they are groundless, but also brought forward further and convincing evidence that the substance described by him as dihydro(anhydro)-berberine is in fact that substance.

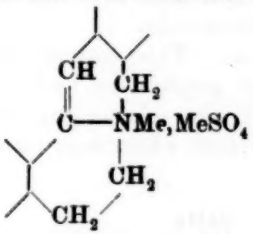
The results of the present investigation indirectly confirm the identity of dihydroanhydroberberine, and additional positive evidence has arisen from the observation that it is possible to grow crystals of this substance and also of tetrahydroanhydroberberine from acetone which are suitable for crystallographical examination. The measurement of these crystals, which was kindly undertaken by Miss M. W. Porter (p. 741), clearly proves that these substances cannot possibly be identical.

In only one point does the experience of the author in connexion with dihydroanhydroberberine differ from the accurate statements of Gadamer. Gadamer frequently mentions that this base and its salts are easily oxidised by exposure to air and converted into berberine and its salts. The present author, on the other hand, cannot confirm this ready oxidisability. A specimen of the pure hydrochloride which had remained on porous porcelain in a drawer exposed to air for more than six months yielded the same analytical results as before exposure, and the solution of a weighed quantity in water gave, on the addition of ammonia, a precipitate of dihydroanhydroberberine which was nearly the amount which should have been obtained from the pure hydrochloride (p. 740). If conversion of the hydrochloride into berberinium chloride had taken place during exposure, there would either have been no precipitate on the addition of ammonia or, in the event of partial change, a diminished yield. Again, a specimen of pure dihydroanhydroberberine which had been several times recrystallised from acetone and melted at 167—168° was left on a watch-glass exposed to the air for six months without apparent change. At the end of this time, the specimen melted at the same temperature as before exposure and yielded the same analytical results, an experience which is in accord with the statement of Gadamer that a specimen of dihydroanhydroberberine, crystallised from ether, which he had prepared in 1902, still showed the same melting point in 1910 as when first prepared. It seems therefore clear that dihydroanhydroberberine is not readily oxidised by contact with air, and this is in harmony with the behaviour observed in the analogous case of

dihydroanhydro*epi*berberine (this vol., p. 507), which also may be exposed to the air for a long time without apparent change.

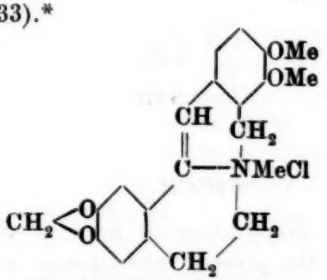
Dihydroanhydroberberine Methosulphate and its Conversion into Anhydromethylberberine.

The basis of the experiments chronicled in the following pages is *dihydroanhydroberberine methosulphate* (p. 743),

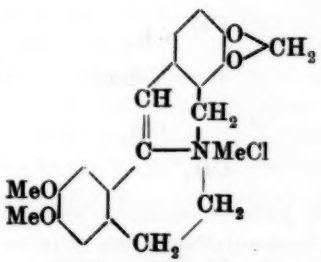


which is readily prepared by the direct combination of dihydroanhydroberberine with methyl sulphate, and separates from methyl alcohol in brilliant yellow, orthorhombic prisms melting at 205°.

The corresponding *methiodide*, $C_{20}H_{19}O_4N$,MeI (m. p. 215—220°), which is obtained from the methosulphate by precipitation with potassium iodide, had already been described by Freund and Fleischer (*Annalen*, 1915, **409**, 231), who prepared it by the direct addition of methyl iodide to dihydroanhydroberberine. *Dihydroanhydroberberine methochloride*, $C_{20}H_{19}O_4N$,MeCl (m. p. 223°), obtained by digesting the iodide with water and silver chloride, separates from water, apparently with $5H_2O$, in pale yellow prisms. This methochloride has been made the subject of special inquiry on account of its close relationship to *iso*cryptopine chloride (833).*



Dihydroanhydroberberine methochloride.



*iso*Cryptopine chloride.

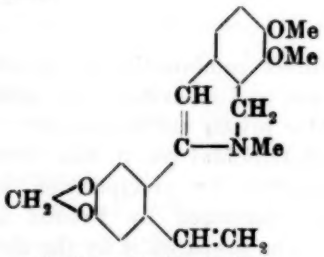
These so closely allied quaternary chlorides exhibit, as was to be expected, great similarity in their properties and reactions. They

* The numbers in brackets—thus (833)—refer to the paper on Cryptopine and Protopine (T., 1916, **109**, 815–1028).

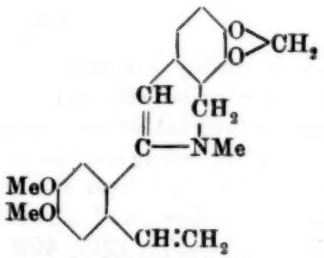
are both characterised by sparing solubility in dilute hydrochloric acid, although dihydroanhydroberberine methochloride is more readily soluble both in water and dilute hydrochloric acid than *iso*cryptopine chloride.

Interesting results have been obtained from the study of the reduction of dihydroanhydroberberine methochloride, and these are described on p. 732. The behaviour of *iso*cryptopine chloride under the same conditions has also been investigated, and will form the subject of a future communication.

Anhydromethylberberine.—This interesting substance corresponds in its method of preparation and in its properties with anhydrocryptopine (850), the relationship between the two substances being at once evident when their formulæ are written side by side:

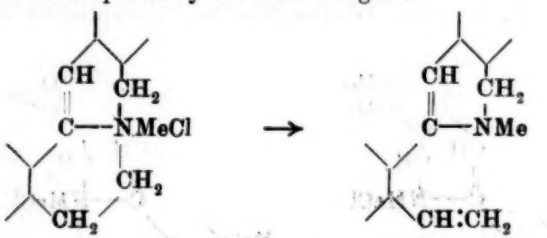


Anhydromethylberberine.



Anhydrocryptopine.

Just as anhydrocryptopine results from the action of methyl-alcoholic potassium hydroxide on *iso*cryptopine chloride, so dihydroanhydroberberine methochloride yields anhydromethylberberine when it is decomposed by the same reagent:

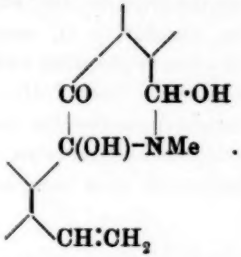


The process actually used in the preparation of most of the anhydromethylberberine required for the present investigation was the direct decomposition of dihydroanhydroberberine methosulphate by boiling with methyl-alcoholic potassium hydroxide (p. 746).

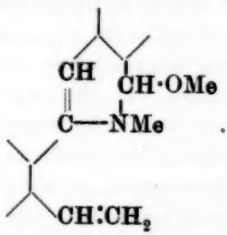
Anhydromethylberberine, $C_{21}H_{21}O_4N$, melts at 94—95° (anhydrocryptopine at 110—111°) and separates from methyl alcohol in pale yellow prisms.

Like anhydrocryptopine, it is a rather weak base, since the

acetate, for example, is dissociated by water, but the salts with mineral acids are stable in the presence of excess of acid. It undergoes a curious change when its solution in methyl alcohol is slowly evaporated in contact with air, yielding, besides a large quantity of a brittle resin, a small amount of a crystalline substance, $C_{21}H_{21}O_7N$ (p. 747), which melts at 153—155°, has no basic properties, and is probably a *trioxyanhydromethylberberine* containing the grouping:

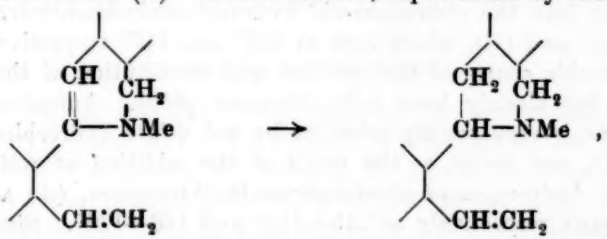


In this respect, anhydromethylberberine appears to behave differently from anhydrocryptopine, since the latter, when boiled with methyl alcohol in contact with air, yields by the addition of methyl alcohol and simultaneous oxidation, large quantities of the two isomeric methoxyanhydrocryptopines (*A*) and (*B*) (856), which contain the grouping:



It is, of course, possible that substances corresponding with the two modifications of methoxyanhydrocryptopine are contained in the resin which is the main product of the action of methyl alcohol and air on anhydromethylberberine, but attempts to isolate such substances in a crystalline condition have been unsuccessful.

Reduction of Anhydromethylberberine to N-*Methyl*isotetrahydro*anhydroberberine* (*B*).—This reduction, represented by the scheme



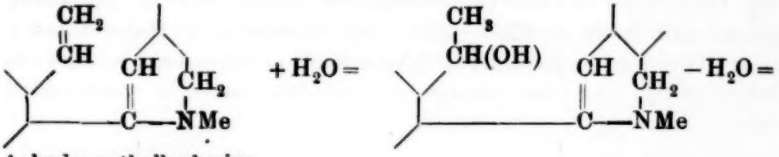
corresponds exactly with the reduction of anhydrocryptopine (989) to anhydrodihydrocryptopine (*B*). The addition of hydrogen takes place readily when the solution of anhydromethylberberine in dilute sulphuric acid is treated with sodium amalgam (p. 748), and, on adding ammonia, a base separates which melts at 112—113° and is identical with *N*-methyl*iso*tetrahydroanhydroberberine (*B*) which Pyman (T., 1913, **103**, 827) obtained from tetrahydroanhydroberberine methohydroxide by evaporation under atmospheric pressure. The similarity in constitution and properties between the anhydrodihydrocryptopines and *N*-methyl*iso*tetrahydroanhydroberberines has already been fully discussed (841), and the preparation of dihydroanhydroberberine methochloride and its conversion first into anhydromethylberberine and then into *N*-methyl*iso*tetrahydroanhydroberberine now completes the picture.

The Action of Hydrochloric Acid on Anhydromethylberberine.

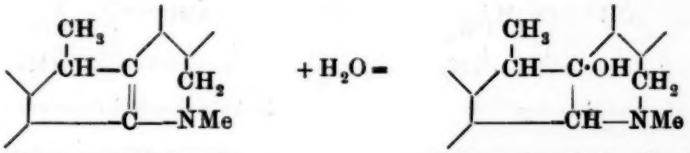
*Formation of the Hydroxy*iso*anhydrodihydromethylberberines (A) and (B).*

A highly characteristic property of anhydrocryptopine is the brilliant crimson colour which is produced when this substance is boiled with *concentrated* hydrochloric acid (865), and the same colour is produced in less degree when anhydromethylberberine is treated in the same manner. In the case of the action of concentrated hydrochloric acid on anhydrocryptopine, it was found possible to isolate two crystalline products, namely, the *epi*cryptopines (*A*) and (*B*), but attempts to obtain similar products in a crystalline condition from the product of the interaction of anhydromethylberberine and concentrated hydrochloric acid have been unsuccessful. On the other hand, another reaction, highly characteristic of anhydrocryptopine, namely, its behaviour towards *dilute* hydrochloric acid, is reproduced exactly when anhydromethylberberine is subjected to the action of dilute hydrochloric acid under the same conditions. When anhydrocryptopine is heated with dilute hydrochloric acid (860), it is converted, by the addition of water into the stereoisomeric hydroxy*iso*anhydrodihydrocryptopines (*A*) and (*B*), which melt at 227° and 117° respectively, and the probable course of the reaction and constitution of these substances has already been fully discussed (862). Anhydromethylberberine is very readily acted on by hot *dilute* hydrochloric acid (p. 752), and yields, as the result of the addition of water, two isomeric *hydroxy*iso*anhydrodihydromethylberberines*, (*A*) and (*B*), which melt respectively at 210—212° and 168—170°. Since these

substances behave in all their properties exactly like the hydroxy-*iso*anhydrodihydrocryptopines, there can be little doubt that they also are stereoisomeric, and that their formation may be expressed by the scheme:



Anhydromethylberberine.



*iso*Anhydromethylberberine. Hydroxy*iso*anhydrodihydromethylberberine (*A*) and (*B*).

The hydroxy*iso*anhydrodihydromethylberberines (*A*) and (*B*) react very readily with acetyl chloride, and the result of the interaction is the same in either case. The product is a mixture of the hydrochlorides, $C_{21}H_{22}O_5NAc,HCl$, of two acetoxy*iso*anhydrodihydromethylberberines, one of which is more readily soluble than the other. The more sparingly soluble hydrochloride (m. p. 253°) yields, on decomposition with ammonia, the acetyl derivative, $C_{21}H_{22}O_5NAc$, which melts at 165—167°, together with some hydroxy*iso*anhydrodihydromethylberberine (*A*) produced by hydrolysis. It would therefore appear that the substance melting at 165—167° is *acetoxy*iso*anhydrodihydromethylberberine* (*A*).

The more readily soluble hydrochloride gives, with ammonia, an acetyl base, $C_{21}H_{22}O_5NAc$, which melts at 213—215°, and is presumably *acetoxy*iso*anhydrodihydromethylberberine* (*B*). It is, however, difficult to be certain as to the identity of these acetyl derivatives, since, on boiling with dilute hydrochloric acid, both yield a mixture of the two hydroxy*iso*anhydrodihydromethylberberines (*A*) and (*B*).

iso*Anhydromethylberberine.*

In connexion with the investigation of the hydroxy*iso*anhydrodihydrocryptopines (*A*) and (*B*) (861), it was pointed out that one of the most characteristic properties of these stereoisomerides is the conversion into *iso*anhydrocryptopine (m. p. 158—160°), a change which both undergo when they are boiled with concentrated

hydrochloric acid or digested with phosphoryl chloride. The (*A*) and (*B*) modifications of hydroxy*iso*anhydrodihydromethylberberine behave in an exactly similar manner (p. 756) and yield *iso*anhydromethylberberine, $C_{21}H_{21}O_4N$, which, like the corresponding cryptopine derivative, crystallises beautifully in glistening prisms and melts at 123—124°. The formation of this substance from the hydroxy*iso*anhydrodihydromethylberberines is due to dehydration, and the change is probably correctly represented thus:

Hydroxy*iso*anhydrodihydromethylberberine. → *iso*Anhydromethylberberine.

iso*Anhydromethylberberine* yields well-defined, sparingly soluble salts, of which the hydrochloride, $C_{21}H_{21}O_4N,HCl$ (m. p. 205—210°), and the hydriodide, $C_{21}H_{21}O_4N,HI$ (m. p. 247°), were prepared and analysed.

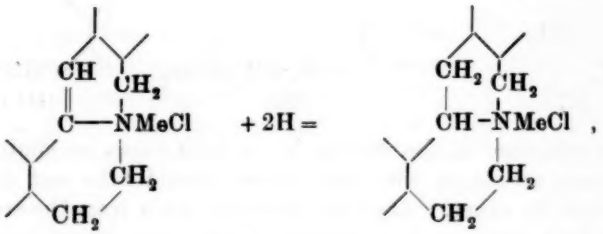
When the sulphate is boiled with excess of dilute sulphuric acid, hydration occurs, and two substances, $C_{21}H_{23}O_5N$, are produced which melt at 215° and 165—167° respectively.

These consist of the (*A*) and (*B*) modifications of hydroxy*iso*anhydrodihydromethylberberine, and the production of these modifications, in this manner, is strong evidence that the view of their formation from anhydromethylberberine advanced on p. 731 is correct.

Reduction of Dihydroanhydroberberine Methochloride.

The interesting behaviour of dihydroanhydroberberine methochloride on reduction in boiling dilute hydrochloric acid solution with sodium amalgam has been made the subject of an extended investigation (p. 758), partly with the view of comparing the results with those obtained from the study of the reduction of *iso*cryptopine chloride under the same conditions, an investigation which it is hoped will form the subject of a future communication. Under the conditions mentioned, dihydroanhydroberberine methochloride yields a quaternary chloride (*a*) and the hydrochloride (*b*) of a new base. The quaternary chloride (*a*), produced by the addition of two atoms of hydrogen to the double linking, can be separated by fractional crystallisation into two substances melting at 245—250° and 280—285° respectively, and these are identical with

the (α-) and (β-) modifications of the methochloride of tetrahydroanhydroberberine first prepared by Pyman (T., 1913, **103**, 825, 826) by the addition of methyl iodide to tetrahydroanhydroberberine and subsequent treatment with silver chloride. The reduction of dihydroanhydroberberine methochloride in this case has therefore proceeded in a simple manner according to the scheme:

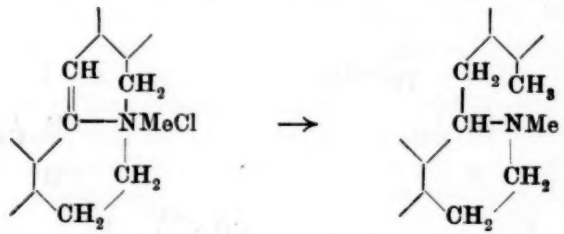


a process which creates an asymmetric carbon atom, and thus allows of the formation of stereoisomeric methochlorides, because the molecule already contains an asymmetric centre, namely, the nitrogen atom attached to five different groups.

The base from the hydrochloride (*b*) is a syrup, has the composition $C_{21}H_{25}O_4N$, and has therefore been produced from dihydroanhydroberberine methochloride according to the equation

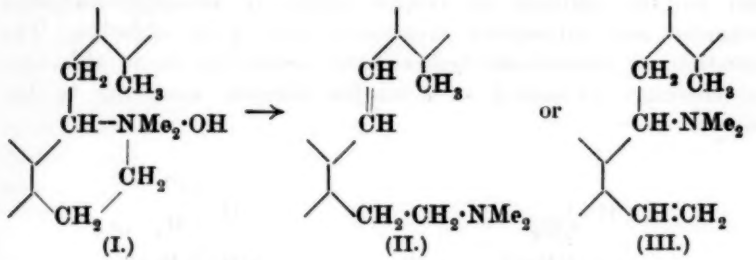
$$C_{20}H_{19}O_4N,MeCl + 7H = C_{20}H_{25}O_4NMe + HCl.$$

The comparison of the properties of this base with those of a similar but better characterised base, which has been obtained by the reduction of *iso*cryptopine chloride, leaves little doubt that its formation is correctly expressed in the following manner:



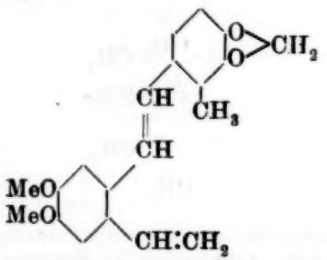
This base is therefore *dihydromethylisotetrahydroanhydroberberine* (compare Pyman, T., 1913, **103**, 828). It combines readily with methyl sulphate, and the resulting methosulphate is decomposed by boiling with methyl-alcoholic potassium hydroxide (p. 760), with the formation of *dihydrodimethylisotetrahydroanhydroberberine*, $C_{22}H_{27}O_4N$ (950). There are two directions in which the elimination of water from the methohydroxide (I) may

take place, leading to the formation of substances represented by formulæ II or III:

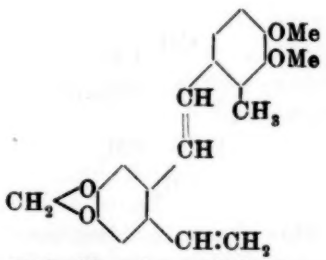


The mechanism of the change is, in both cases, so similar that there seems no reason why the process should take one direction rather than the other. Arguing, however, again from the analogous behaviour of *iso*cryptopine chloride in the same circumstances—in which case it has been clearly demonstrated that the substance produced by the elimination of water from the methohydroxide corresponding with I has formula II, and not III—there is every reason to suppose that the formula of dihydrodimethyl*iso*tetrahydroanhydroberberine is that represented by II. This syrupy base yields a crystalline methosulphate, $C_{22}H_{27}O_4N,Me_2SO_4$, which, on boiling with methyl-alcoholic potassium hydroxide, readily loses trimethylamine and water and yields a beautifully crystalline substance, $C_{20}H_{20}O_4$, which melts at 113—114°.

Careful investigation of this substance has shown that it is completely analogous to cryptopidene (827), and it has therefore been named '*berberidene*.' The intimate relationship between these two substances is well brought out when their formulæ are written side by side:



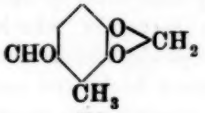
Cryptopidene (m. p. 124°).



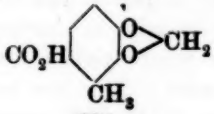
Berberidene (m. p. 114°).

The main evidence in support of the formula assigned to cryptopidene was derived from the study of its behaviour on oxidation, when it yielded 5:6-methylenedioxy-*o*-tolualdehyde (I) and 5:6-methylenedioxy-*o*-toluic acid (II) from the upper part of the mole-

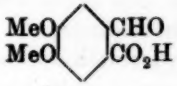
cule and 4:5-dimethoxy-2-aldehydobenzoic acid (*m*-opianic acid, III) from the lower section:



(I.)

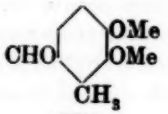


(II.)

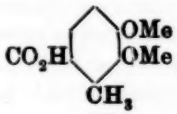


(III.)

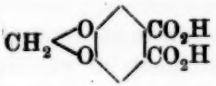
When berberidene was subjected to oxidation, in acetone solution with permanganate (p. 762) in exactly similar circumstances, it yielded 5 : 6-dimethoxy-*o*-tolualdehyde (IV), 5 : 6-dimethoxy-*o*-toluic acid (V), from the upper, and an acid melting at 174—176°, which was doubtless hydrastic acid (VI), from the lower part of the molecule:



(IV.)



(V.)

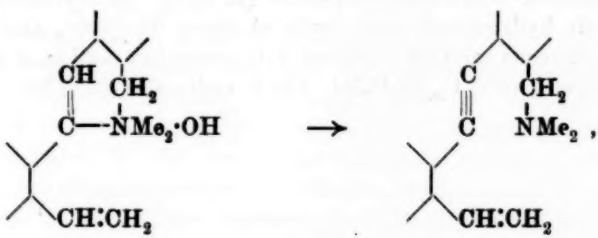


(VI.)

The formation of these substances is obviously in complete harmony with the constitution assigned above to berberidene.

Anhydromethylberberine Methosulphate and ψ-Methylberberinium Chloride.

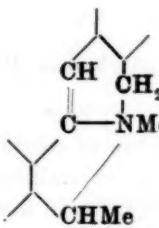
Anhydrocryptopine combines readily with methyl sulphate, yielding a colourless, crystalline methosulphate (978) which resembles other methosulphates in many of its reactions, but is characterised by the remarkable fact that it is decomposed by alkalis with regeneration of anhydrocryptopine, whereas normally the methyl derivative should have resulted. Attempts to explain the unusual course of this decomposition were made at the time (854), but it was not then pointed out that if the reaction had proceeded normally it would have led to the formation of a substance containing a triple bond, and it is possible that the disinclination to



form such a substance may be very great and is perhaps a factor in bringing about the abnormal decomposition of the methosulphate.

In view of the unusual properties exhibited by anhydrocryptopine methosulphate, it was clearly of interest to ascertain whether anhydromethylberberine would yield a methosulphate which would behave in a similar manner. This has been found to be the case. Anhydromethylberberine, $C_{21}H_{21}O_4N$, combines readily with methyl sulphate, and the resulting methosulphate, $C_{21}H_{21}O_4N,Me_2SO_4,H_2O$, crystallises from water in colourless needles melting at 150—152°. The *methiodide*, $C_{21}H_{21}O_4N,MeI$, obtained from the methosulphate by precipitation with potassium iodide, closely resembles anhydrocryptopine methiodide in appearance and general properties, and it is curious that both melt at the same temperature (188—190°). When anhydromethylberberine methosulphate is digested with methyl-alcoholic potassium hydroxide, decomposition occurs readily and a substance separates which, after crystallisation from methyl alcohol, melts at 92—94° and consists of anhydromethylberberine, the yield being almost quantitative. In this decomposition, anhydromethylberberine methosulphate behaves in precisely the same unusual way as anhydrocryptopine methosulphate.

ψ-Methylberberinium Chloride,



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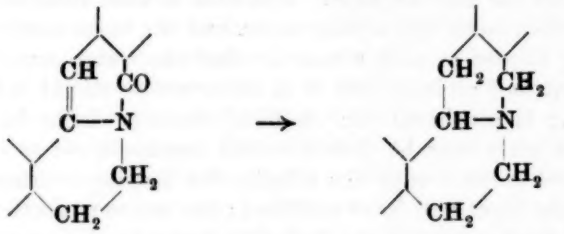
Just as ψ-cryptopine chloride (m. p. 110°) results from the action of boiling concentrated hydrochloric acid on anhydrocryptopine methosulphate (984), so the same process applied to anhydromethylberberine methosulphate leads to the formation of *ψ-methylberberinium chloride*, $C_{21}H_{22}O_4NCl,H_2O$. This interesting quaternary chloride closely resembles ψ-cryptopine chloride in its curious colour reactions and other properties (p. 751). It crystallises well from dilute hydrochloric acid, melts at about 95—100°, and yields, when its aqueous solution is mixed with potassium iodide, *ψ-methylberberinium iodide*, $C_{21}H_{22}O_4NI$, which melts at 175—180°.

Reduction of Oxyberberine to Tetrahydroanhydroberberine,



The synthesis of oxyberberine was accomplished by Pictet and Gams in 1911 (*Compt. rend.*, **152**, 1102), but as these investigators were unable to reduce oxyberberine to tetrahydroanhydroberberine, which, on oxidation in acid solution, would in turn yield salts of berberine, they were obliged to devise another method in order to complete the synthesis of the salts of berberine (*Compt. rend.*, 1911, **153**, 386; *Ber.*, 1911, **44**, 2480). The present author finds, however, that oxyberberine may be readily reduced electrolytically to tetrahydroanhydroberberine under the conditions given on p. 764. It follows, therefore, that the synthesis of oxyberberine by Pictet and Gams is now also a synthesis of berberine

Experimental.

The Action of Sodium Hydroxide on Berberinium Chloride.

Preparation of Oxyberberine and Dihydroanhydroberberine.

The conversion of berberinium sulphate into oxyberberine and dihydroanhydroberberine by heating with sodium hydroxide was first observed by Gadamer (*Arch. Pharm.*, 1905, **243**, 35), and at a later date (*ibid.*, 1910, **248**, 676) more complete details of the process and of the isolation of the products were given by the same investigator. The method recommended is, however, a tedious one and has the disadvantage that the isolation of the products not only entails a large number of operations, but necessitates the use of large volumes of ether.

Since considerable quantities of dihydroanhydroberberine were required for the present research, the author has carried out a series of comparative experiments on the action of sodium hydroxide on berberinium chloride (which is more accessible than the sulphate), and, as the result, the following procedure has been adopted for the preparation of dihydroanhydroberberine and oxyberberine. Commercial berberine hydrochloride (berberinium

chloride, 500 grams) is thoroughly mixed with aqueous sodium hydroxide (700 c.c. of 30 per cent.) in a stout, round-bottomed flask and left for half an hour. The flask is then suspended in a large enamelled basin full of cold water, and the basin slowly heated over a ring burner in such a manner that the water comes to the boil in about half an hour, and it is better not to stir at this stage. The heating is continued for an hour, during which the viscid, dark brown mass may be shaken round repeatedly so as to bring it into better contact with the alkali. On keeping overnight, the black, syrupy layer will have solidified; the aqueous alkali is then run off, the mass washed in the flask with water by decantation, and mixed with dilute hydrochloric acid until the whole is strongly acid. After heating on the steam-bath and filtering by the aid of the pump, the residue is ground up and the treatment with hot dilute hydrochloric acid repeated until all the basic substance has been extracted and a nearly colourless mass of oxyberberine remains.

The different extracts are mixed, while still hot, with concentrated hydrochloric acid, when, on keeping, a large crop of crystals separates which consists of the hydrochloride of dihydroanhydroberberine mixed with varying quantities of unchanged berberinium chloride.

The crops of crystals from the hydrochloric acid extracts, obtained as described above, are collected, washed with dilute hydrochloric acid to remove the dark greenish-brown solution, and recrystallised by dissolving in the least quantity of boiling water and adding concentrated hydrochloric acid. After being collected, the crystals are dissolved in hot water and mixed with excess of ammonia, when a dark brown, semi-solid mass separates which soon hardens. This is ground up and washed by the aid of the pump with hot water until the filtrate is no longer dark purplish-brown;* the residue is then left on porous porcelain until dry. In order to

* The intensely coloured filtrate deposits, on keeping, a splendid chocolate coloured salt which crystallises from hot water in brilliant chocolate coloured needles and was at first thought to be a new substance. In this condition the salt had the remarkable property of dissolving in boiling dilute hydrochloric acid to an orange solution and separating in deep orange needles. Even after repeated recrystallisation from dilute hydrochloric acid, the salt retained the peculiarity of dissolving in boiling dilute ammonia to an intense purple solution from which chocolate coloured needles separated on cooling. However, after repeated crystallisation from methyl alcohol, the salt lost this property and was found to consist of berberinium chloride, since it yielded oxyberberine and dihydroanhydroberberine with sodium hydroxide. The methyl-alcoholic mother liquors contain the highly coloured substance and, when the solution is concentrated, this separates, mixed with berberinium chloride, in almost black needles, the nature of which has not been determined.

purify this crude dihydroanhydroberberine, the best plan is to triturate it with methyl alcohol, in which it is sparingly soluble, then to transfer to the filter and wash with methyl alcohol until the intensely red impurity has been removed, and finally to repeat the same process with acetone. The residue melts at 163—166° and is dihydroanhydroberberine of good quality; after two crystallisations from acetone the substance is quite pure (m. p. 168—170°). The acetone liquors from the washing and crystallisations of the crude dihydroanhydroberberine yield, on concentration, a further crop, which is, however, very dark coloured, and the better plan is to distil off the acetone and dissolve the dark syrup in boiling dilute hydrochloric acid. The solution is mixed with concentrated hydrochloric acid, the hydrochloride which separates on keeping is recrystallised and worked up for dihydroanhydroberberine exactly as already described. Since Faltis (*Monatsh.*, 1910, **31**, 565) has stated that the substance obtained in the decomposition of a berberinium salt with sodium hydroxide is not dihydroanhydroberberine, $C_{20}H_{19}O_4N$, but tetrahydroanhydroberberine, $C_{20}H_{21}O_4N$, three different preparations were analysed:

0·1142 gave 0·2970 CO_2 and 0·0581 H_2O. C = 70·9; H = 5·6.
0·1075 „ 0·2805 CO_2 „ 0·0550 H_2O. C = 71·2; H = 5·7.
0·1161 „ 0·3032 CO_2 „ 0·0591 H_2O. C = 71·3; H = 5·7.

$C_{20}H_{19}O_4N$ requires C = 71·2; H = 5·6.
$C_{20}H_{21}O_4N$ requires C = 70·8; H = 6·2 per cent.

Dihydroanhydroberberine melts, according to Gadamer, at 169—170°, and the specimens used in the above analyses all melted when moderately rapidly heated at 168—170°. An intimate mixture of approximately equal amounts of dihydroanhydroberberine and tetrahydroanhydroberberine (m. p. 170°) softened at 140—145° and was completely melted at 152°, so that there can be no question of their identity.

Dihydroanhydroberberine is sparingly soluble in methyl alcohol or acetone, even on boiling, but dissolves more readily in boiling ethyl alcohol. It is rather readily soluble in boiling benzene, from which it crystallises well in yellow prisms. The solution in acetic acid does not give a characteristic coloration on the addition of sulphuric acid, but the addition of a trace of dilute nitric acid causes a deep brown to develop.

In view of the fact that anhydromethylberberine (p. 730) is so readily changed by boiling with hydrochloric acid, and this substance and dihydroanhydroberberine are so similarly constituted it seemed desirable that the behaviour of dihydroanhydroberberine towards hydrochloric acid should also be investi-

gated. The powdered base dissolves readily when mixed with concentrated hydrochloric acid and heated to boiling by means of a sulphuric-acid bath, and the deep yellow solution becomes paler as the boiling continues. After ten minutes, the hydrochloric acid was boiled off, leaving a yellow syrup which, on the addition of water, immediately crystallised in yellow needles, and these consisted of dihydroanhydroberberine hydrochloride. The solution of the salt in warm water gave with ammonia the free base, which, after crystallisation from methyl alcohol, melted at 168° and consisted of dihydroanhydroberberine.

The Stability of Dihydroanhydroberberine and its Salts when exposed to Air.—It is pointed out in the introduction (p. 726) that Gadamer more than once directs attention to the ready oxidisability of dihydroanhydroberberine and its salts when left in contact with air (for example, *Arch. Pharm.*, 1905, **243**, 37; 1910, **248**, 671, 672, 674), and that the present author is unable to confirm this ready oxidisability. The evidence in support of the stability of dihydroanhydroberberine and its hydrochloride towards atmospheric oxygen is as follows: A specimen of dihydroanhydroberberine which had crystallised from acetone in small crystals and melted at 167—168° was analysed in December, 1917, and yielded C = 71·2, H = 5·7, whereas $C_{20}H_{19}O_4N$ requires C = 71·2, H = 5·6 per cent. This specimen was left on a watch-glass in a large drawer which was in frequent use, fully exposed until the end of June, 1918, when it had not altered in appearance, still melted at 167—168°, and yielded on analysis C = 71·1, H = 5·6. In the second case, dihydroanhydroberberine hydrochloride, prepared from the pure base, was repeatedly recrystallised from dilute hydrochloric acid, and a portion taken and dried at 90°, when it yielded C = 61·5, H = 5·7, whereas $C_{20}H_{19}O_4N,HCl,H_2O$ requires C = 61·3, H = 5·6 per cent. The remainder (14 grams) was left on a porous plate exposed to the air, in the drawer already mentioned, for a like period of about six months, and had then the same brilliant appearance as at first. When a weighed portion was heated at 90° until constant, it lost 12·1 per cent., and the residue gave on analysis C = 61·6, H = 5·7, or almost exactly the same result as before exposure. It may be pointed out that these and other analytical results point to the formula $C_{20}H_{19}O_4N,HCl,4H_2O$ as representing the composition of dihydroanhydroberberine hydrochloride, and show that of the $4H_2O$, one remains at 90°, exactly as in the case of berberinium chloride, for $C_{20}H_{19}O_4N,HCl,4H_2O$, losing $3H_2O$, means a loss of 12·1 per cent., and the formula $C_{20}H_{19}O_4N,HCl,H_2O$ requires C = 61·3, H = 5·6 per cent. Gadamer states that his analytical results point to the formula $C_{20}H_{19}O_4N,HCl,3H_2O$, but

his determinations of water of crystallisation and chlorine* agree fairly well with the formula containing $4H_2O$.

Since there is little difference in composition between berberinium chloride, $C_{20}H_{18}O_4NCl$, and dihydroanhydroberberine hydrochloride, it was still necessary to prove that the salt which had been exposed to the air consisted of the latter substance. For this purpose, the hydrochloride (13·5 grams), dissolved in a little hot water, in which it is readily soluble, was made alkaline with ammonia and allowed to remain until the viscid precipitate had hardened. While still warm, the precipitate was collected, triturated with water, and thoroughly washed; it was then dried on porous porcelain in the steam-oven, and weighed 9·75 grams, whereas the amount of dihydroanhydroberberine which should have been produced from 13·5 grams of the pure hydrochloride, $C_{20}H_{19}O_4N,HCl,4H_2O$, is 10·2 grams. The base on crystallisation from methyl alcohol melted at 166—168°, and was pure dihydroanhydroberberine. The ammoniacal mother liquors gave, on concentration under diminished pressure and admixture with a large excess of hydrochloric acid, a slight crystalline precipitate. On remaining in the ice-chest, this increased somewhat, and, after collecting, washing with dilute hydrochloric acid, and drying in the steam-oven, it weighed 0·55 gram, and consisted of berberinium chloride. Apparently, therefore, oxidation had taken place, but to a very slight degree.

Crystallographical Examination and Comparison of Dihydroanhydroberberine and Tetrahydroanhydroberberine.

It has already been pointed out (p. 725) that Faltis (*Monatsh.*, 1910, **31**, 565) had expressed the opinion that the base obtained by the action of concentrated alkalis on the berberinium salts is not dihydroanhydroberberine, as claimed by Gadamer (*Arch. Pharm.*, 1905, **243**, 35), but is, in fact, tetrahydroanhydroberberine. In order the more effectually to disprove this view, specially pure preparations of the substances in question were made, crystallised from acetone, and several well-developed crystals of each carefully measured.† The author is indebted to Miss Porter and Mr. T. V. Barker for undertaking the measurements.

* There is a slip in the calculation of the chlorine content of $C_{20}H_{19}O_4N,HCl,3H_2O$, which should be 8·3 and not 9·5 per cent.

† Tetrahydroanhydroberberine, prepared by the reduction of berberinium chloride or sulphate with zinc and dilute acid, is rarely obtained colourless, and the crystals retain their colour persistently even after repeated recrystallisation. In order to remove the colour, a good plan is to recrystallise

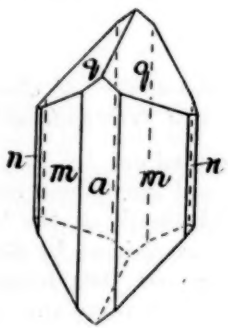
Dihydroanhydroberberine (M. W. Porter).

The crystals are monoclinic with the axial ratios: $a:b:c=1\cdot708:1:0\cdot831$; $\beta = 96°40'$. Determinants: $0\bar{1}\bar{1}/0\bar{1}1/100$. Complex-symbol: $4h;-6\frac{1}{2}/59\frac{1}{2}/-5$. Forms observed: $a\{100\}$, $m\{110\}$, $n\{120\}$, $q\{011\}$. The crystals of this compound are slender, prismatic in habit, as shown in Fig. 1. The form $a\{100\}$ is fairly well developed, but $m\{110\}$ predominates. The faces of the form $n\{120\}$ are narrow. Four fairly good crystals were measured. The results of the measurements are shown below.

		Azimuth (ϕ).		
Face.	No. of readings.	Limits.	Obs.	Calc.
a (100)	7	89°47′—90°12′	89°59′	90°0′
m (110)	10	30 18 —30 40	*30 31	—
n (120)	9	16 30 —17 12	16 48	16 25
q (011)	6	7 35 — 8 14	*8 0	—

		Polar distance (ρ).		
Face.	No. of readings.	Limits.	Obs.	Calc.
a (100)	7	90°0′ —90°8′	90°1′	90°0′
m (110)	10	90 0 —90 0	90 0	90 0
n (120)	9	90 0 —90 0	90 0	90 0
q (011)	6	39 51 —40 6	*40 0	—

FIG. 1.



Tetrahydroanhydroberberine (M. W. Porter).

The crystals are monoclinic and exhibit the forms $o\{111\}$, $o'\{\bar{1}11\}$, $a\{100\}$, and $c\{001\}$, with the octahedral habit shown in Fig. 2. Crystallographic constants: 47°54′, a(48°17′)m(41°43′)b, 50°36′, 89°4′; or, alternatively, $a:b:c=1\cdot121:1:0\cdot904$, $\beta=90°56'$.

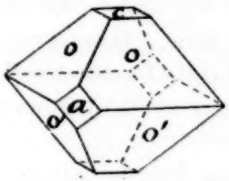
the hydrochloride from glacial acetic acid, in which it is rather sparingly soluble, until the salt is perfectly white and then to liberate the base and crystallise it from alcohol or acetone. Tetrahydroanhydroberberine purified in this way is perfectly colourless and melts at 174°.

Determinants: 010/001/100. Complex-symbol: $4d; +1/59/+3$. Following are the mean observations from three crystals:

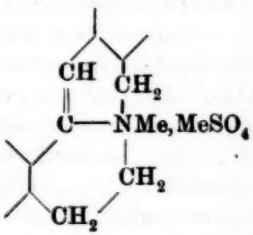
	a (100).	*c* (001).	*o'* ($\bar{1}11$).	*o* (111).	
Azimuth (ϕ)	Face of	90°0′	47°54′	*47°54′	
Polar distance (ρ) ...	reference	*89 4	*120 20½	58 38	(Calc. 58 37)

Although the crystals are pseudo-orthorhombic, an optical examination agreed with monoclinic symmetry.

FIG. 2.



Dihydroanhydroberberine Methosulphate,



This substance may be prepared by adding excess of freshly distilled methyl sulphate (10 c.c.) to a solution of dihydroanhydroberberine (10 grams) in boiling benzene, when there is no immediate precipitate, but gradually the yellow methosulphate separates in prisms. After remaining overnight, the mass is collected, washed with benzene, and dried in the steam-oven, when a yield of 10 grams is obtained, and a further crop of less pure material separates from the concentrated mother liquor. The whole is crystallised from methyl alcohol, in which the methosulphate is sparingly soluble and from which it separates in well-developed prisms. A better method of preparation is to shake the base (10 grams) with methyl sulphate (15 c.c.) in a stoppered bottle, when a thin paste is formed without development of heat. On keeping, the paste gradually becomes thicker, and after eight days combination is complete. The product is triturated with benzene, filtered, and the residue crystallised from methyl alcohol. The comparative slowness of the combination is evidenced by the fact that, if the mass after two days is washed with benzene and boiled with water, only about half dissolves as the methosulphate, and the rest is unchanged dihydro-

anhydroberberine. For analysis, the air-dried substance was dried in the steam-oven, when it lost about 8 per cent.:

0·1168 gave 0·2435 CO_2 and 0·0578 H_2O. C = 56·8; H = 5·5.
$C_{20}H_{19}O_4N,Me_2SO_4$ requires C = 57·0; H = 5·4 per cent.

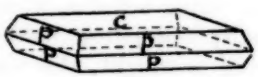
Dihydroanhydroberberine methosulphate shrinks at 140° and melts at about 205° to an amber syrup; it dissolves sparingly in cold, but readily in hot water, and separates as a very voluminous mass of microscopic, lemon-yellow needles which filter with difficulty. The air-dried crystals seem to contain $4H_2O$, since a specimen which had been exposed to the air for ten days gave the following results:

0·1132 lost 0·0147 at 100°. H_2O = 13·0.
$C_{20}H_{19}O_4N,Me_2SO_4,4H_2O$ contains H_2O = 13·3 per cent.
The residue, 0·0985 gave 0·2050 CO_2 and 0·0485 H_2O. C = 56·8; H = 5·5 per cent.

Miss M. W. Porter was kind enough to examine some crystals of dihydroanhydroberberine methosulphate which had been obtained from methyl alcohol, and reports as follows:

The crystals are orthorhombic and exhibit the forms $c\{001\}$ and $p\{111\}$. The habit is tabular, parallel to c (see Fig. 3), which is a plane of perfect cleavage. The mean results of measurement for $p(111)$ are: azimuth $(\phi) = 48°40'$; polar distance $(\rho) = 64°26'$. Axial ratios: $a:b:c = 0·879:1:1·380$. Determinants: 010/100/001. Complex-symbol: $4d/64°26'/+3°40'$.

FIG. 3.



The aqueous solution of the methosulphate gives no precipitate on the addition of ammonia, even on boiling, but hot concentrated sodium hydroxide produces a milky solution from which a white, crystalline precipitate separates. The methosulphate is readily soluble in glacial acetic acid, and the addition of sulphuric acid produces a pink coloration which, on keeping, becomes more intense; a drop of dilute nitric acid changes this to deep claret and then to brown. The benzene washings of the crude methosulphate, as well as the aqueous and methyl-alcoholic mother liquors, contain a second substance, which is much more readily soluble than the methosulphate and can be separated from it by fractional crystallisation from water. The amber prisms obtained in this way, on the addition of ammonia to their aqueous solution,

gave a precipitate of dihydroanhydroberberine, and consist, therefore, evidently of *dihydroanhydroberberine methyl hydrogen sulphate*:

0·1002 gave 0·2055 CO_2 and 0·0475 H_2O. C = 56·0; H = 5·2.

$C_{20}H_{19}O_4N,MeHSO_4$ requires C = 56·1; H = 5·1 per cent.

When any considerable quantity of the crude mixture of methosulphate and methyl hydrogen sulphate accumulates, a good plan is to dissolve the whole in boiling water and add ammonia. The dihydroanhydroberberine which separates is rapidly collected, and is remarkably pure, whilst the hot filtrate, on keeping, deposits the pure methosulphate.

Dihydroanhydroberberine Methiodide, $C_{20}H_{19}O_4N,MeI$.—A boiling dilute solution of dihydroanhydroberberine methosulphate gives, on the addition of boiling dilute potassium iodide, a clear solution, from which the iodide immediately begins to crystallise as a lemon-yellow powder:

0·1175 gave 0·2265 CO_2 and 0·0472 H_2O. C = 52·6; H = 4·5.

$C_{21}H_{22}O_4NI$ requires C = 52·6; H = 4·5 per cent.

This iodide darkens rapidly above 190°, is brick-red at about 200°, and melts at about 215—220° with effervescence to a reddish-brown froth. It is very sparingly soluble in water, but comparatively readily so in boiling alcohol, from which it separates in thin, microscopic plates. This methiodide is evidently identical with the substance which Freund and Fleischer (*Annalen*, 1915, **409**, 231) obtained from dihydroanhydroberberine by the direct action of methyl iodide, which they found to melt at 223—224°.

The *methochloride*, $C_{20}H_{19}O_4N,MeCl$, was obtained by grinding the iodide to a paste with water, adding much water and freshly precipitated silver chloride, and heating on the water-bath for an hour. After filtering, the almost colourless solution was concentrated and allowed to remain, when a crust of glistening, well-developed, four-sided prisms separated, which were collected, ground, and allowed to remain exposed to the air for a week. The substance appears to contain $5H_2O$, of which $4H_2O$ are removed by drying at about 95°:

0·1287 lost 0·0229 at 95°. H_2O = 17·7.

$C_{21}H_{22}O_4NCl,5H_2O$ losing $4H_2O$ requires H_2O = 18·1.

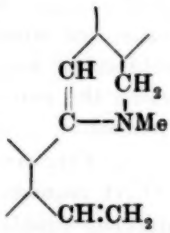
After drying at 90°, 0·1267 gave 0·2890 CO_2 and 0·0671 H_2O. C = 61·8; H = 5·9.

$C_{21}H_{22}O_4NCl,H_2O$ requires C = 62·1; H = 5·9 per cent.

Dihydroanhydroberberine methochloride melts and decomposes at about 223° with evolution of gas to a brown syrup. It is sparingly soluble in cold, but readily so in boiling water, and a drop of the

solution mixed with dilute sulphuric acid gives, on the addition of a trace of manganese dioxide, a pink coloration which, on boiling, becomes claret coloured. It dissolves readily in hot glacial acetic acid and crystallises, on cooling, in needles. The addition of sulphuric acid to the solution of a crystal in a drop of glacial acetic acid produces an intense purple coloration. When the methochloride is heated in a drawn-out test-tube by means of a sulphuric-acid bath at 230° for a couple of minutes, methyl chloride is eliminated, and the solution of the dark brown residue in boiling methyl alcohol deposits pale brown crystals which melt at about 165—167°, and consist of dihydroanhydroberberine (compare this vol., p. 506).

Anhydromethylberberine,



Anhydromethylberberine is obtained when dihydroanhydroberberine methosulphate is digested with methyl-alcoholic potassium hydroxide, and it is important that the methosulphate should be quite free from dihydroanhydroberberine methyl hydrogen sulphate, otherwise the anhydromethylberberine will be contaminated with dihydroanhydroberberine, and then very difficult to purify. The methosulphate should therefore be recrystallised from methyl alcohol until its aqueous solution, on the addition of ammonia, remains perfectly clear, even on warming. The methosulphate (5 grams), dissolved in the least possible quantity of boiling methyl alcohol, is mixed with methyl-alcoholic potassium hydroxide (30 c.c. of 25 per cent.) and vigorously boiled, so that much of the methyl alcohol escapes. The clear solution soon clouds, and oily drops separate which sink to a yellow globule at the bottom of the vessel. After ten minutes, the whole is vigorously shaken under cold water in order to granulate the mass, water is added, the rather viscid precipitate collected, washed with water, and ground and washed with methyl alcohol, which removes a good deal of oily impurity and leaves a pale yellow, crystalline mass. Finally, the substance is rapidly crystallised from methyl alcohol or acetone. Difficulty was experienced in obtaining good analytical results until a lead chromate tube was employed:

0·1001 gave 0·2625 CO_2 and 0·0548 H_2O. C = 71·5; H = 6·1.
0·1012 „ 0·2664 CO_2 „ 0·0551 H_2O. C = 71·8; H = 6·1.

$C_{21}H_{21}O_4N$ requires C = 71·8; H = 6·0 per cent.

Anhydromethylberberine melts at 94—95°, and, like anhydrocryptopine (m. p. 110—111°, p. 975), is sparingly soluble in methyl alcohol, from which it crystallises, if the operation is carried out rapidly and with small quantities (see below), in fern-like groups of needles; it separates from acetone, in which it is readily soluble, in pale yellow prisms. Unfortunately, these are striated, and therefore unsuitable for measurement and comparison with the crystals of anhydrocryptopine (976).

Anhydromethylberberine is a weak base, since its bright yellow solution in glacial acetic acid is precipitated by water, and it does not dissolve in very dilute hydrochloric acid in the cold.

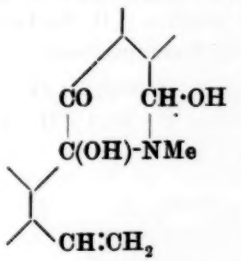
A trace of the substance dissolved in a drop of acetic acid gives with sulphuric acid a faint yellowish-brown solution which rapidly becomes chartreuse-green, and the addition of a trace of dilute nitric acid changes the colour to bright cherry-red.

If benzenediazonium chloride is added to the solution in acetic acid, a deep orange-red coloration is produced, and precisely the same reaction is shown by anhydrocryptopine.

When boiled with methyl alcohol in contact with the air, anhydromethylberberine rapidly undergoes some profound change, since, although it is very sparingly soluble in this solvent in the cold, only a comparatively small part separates on keeping, particularly if the experiment has been carried out with large quantities of material and there is no further separation on concentrating the dark brown mother liquor. When the mother liquors from a number of crystallisations were allowed to remain in a flask exposed to the air, a crystalline crust gradually separated, and in some cases—notably when pure anhydromethylberberine had been recrystallised—the new substance separated in rosettes of garnet prisms, but the amount was always very small (990):

0·1039 gave 0·2393 CO_2 and 0·0511 H_2O. C = 62·8; H = 5·4.
$C_{21}H_{21}O_7N$ requires C = 63·1; H = 5·3 per cent.

This substance, which apparently contains the grouping



and for which the name *trioxyanhydromethylberberine* is suggested, melts at 153—155° and is a very feeble base, since it does not dis-

solve in cold dilute hydrochloric acid; on boiling, decomposition appears to occur and a milky liquid is produced. The solution in glacial acetic acid is almost colourless, but becomes deep orange when mixed with sulphuric acid, and the addition of a trace of dilute nitric acid produces a dark brown coloration. The dark brown methyl-alcoholic mother liquors from which this substance had separated contained a large amount of a resinous substance, the nature of which has not been investigated.

Reduction of Anhydromethylberberine to N-*Methylisotetrahydroanhydroberberine* (*B*).—This reduction was carried out under the following conditions: Anhydromethylberberine, dissolved in warm concentrated hydrochloric acid or dilute sulphuric acid (20 per cent.), was immediately mixed with ice in a flat basin standing on powdered ice; a large excess of 4 per cent. sodium amalgam was then added, care being taken to keep the liquid strongly acid throughout the operation. If hydrochloric acid has been employed, the sparingly soluble hydrochloride of *N*-methyl*iso*tetrahydroanhydroberberine will have separated, and this is collected and recrystallised from much water or, better, dilute acetic acid.

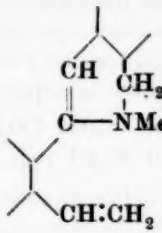
In the case of the use of sulphuric acid, which seems to lead to a rather better yield, the base is precipitated with ammonia, dissolved in dilute hydrochloric acid, and the hydrochloride recrystallised.

The pure hydrochloride is then decomposed and the base several times crystallised from methyl alcohol. (Found: C = 71·1; H = 6·5. $C_{21}H_{23}O_4N$ requires C = 71·4; H = 6·6 per cent.)

This substance melts at 113—115°, and was shown, by direct comparison, to be identical with *N*-methyl*iso*tetrahydroanhydroberberine (*B*), which Pyman (T., 1913, **103**, 827, 835) obtained by the dehydration of tetrahydroanhydroberberine methohydroxide. The *hydriodide*, $C_{21}H_{23}O_4N,HI$, which does not appear to have been described, was prepared by adding boiling dilute potassium iodide to the boiling solution of the hydrochloride, when there was no immediate precipitate, but, on keeping, the hydriodide separated in rather indefinite balls of needles. It darkens at 220° and melts rather sharply at 225° with decomposition:

0·1005 gave 0·1938 CO_2 and 0·0461 H_2O. C = 52·6; H = 4·5.
$C_{21}H_{24}O_4NI$ requires C = 52·4; H = 4·9 per cent.

Anhydromethylberberine Methosulphate,



In preparing this substance, anhydromethylberberine (15 grams) was mixed with methyl sulphate (20 c.c.) in a bottle and well shaken, when the feebly basic nature of the substance was evidenced by the fact that there was no rise of temperature and no apparent immediate action. During twenty-four hours much had dissolved, and gradually the whole became a viscid syrup which, on further shaking, set to a semi-solid mass. After seven days, the mass was triturated with benzene, collected, washed with benzene, and left exposed until free from the solvent. It was then dissolved in boiling water, from which it separated readily in leaflets, and once it is recrystallised it becomes sparingly soluble in water. On keeping exposed to the air, the crystals lose their lustre, but the air-dry substance does not lose weight in the steam-oven, although it still appears to contain $1H_2O$:

0·1218 gave 0·2508 CO_2 and 0·0652 H_2O. C = 56·1; H = 5·9.

$C_{21}H_{21}O_4N,Me_2SO_4,H_2O$ requires C = 55·8; H = 5·7 per cent.

Anhydromethylberberine methosulphate melts at about 150—152° with vigorous effervescence, due to the escape of steam, and the brown syrup, which remains, dissolves in hot water and separates on cooling in white leaflets. It crystallises from water in colourless, flat needles, and is readily soluble in boiling methyl alcohol, from which it separates in groups of thin plates. A trace of the substance dissolved in a drop of glacial acetic acid gives, with sulphuric acid, a pink solution, and a drop of dilute nitric acid added to this changes the colour first to intense blue and then to brown.

When the solution in boiling methyl alcohol is mixed with methyl-alcoholic potassium hydroxide and heated on the steam-bath, it soon becomes milky, and an oil separates after a few minutes. The product was mixed with water, the viscid precipitate collected, washed, and dissolved in boiling methyl alcohol, from which, on rubbing with a glass rod, minute yellow prisms separated which melted at 92—94°, and consisted of anhydromethylberberine (979).

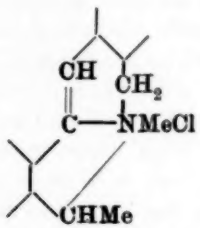
Anhydromethylberberine Methiodide, $C_{21}H_{21}O_4N,MeI$.—When

boiling dilute potassium iodide is added to the boiling dilute solution of the methosulphate, a clear solution is obtained, and remains for some time, but, on rubbing with a glass rod, the iodide immediately commences to separate in groups of flat prisms:

0·1040 gave 0·2052 CO_2 and 0·0461 H_2O. C=53·7; H=4·9.
$C_{22}H_{24}O_4NI$ requires C=53·5; H=4·9 per cent.

This methiodide becomes brown at 185° and melts at 188—190° with vigorous decomposition to a brown froth (980). It is comparatively readily soluble in boiling water, but sparingly so in the cold, and the hot solution, on cooling, becomes milky and then crystallises. It is rather readily soluble in boiling alcohol and separates in groups of striated plates.

ψ-Methylberberinium Chloride,



This interesting substance is obtained from anhydromethylberberine methosulphate by the action of concentrated hydrochloric acid (984).

The methosulphate (1 gram), dissolved in concentrated hydrochloric acid (3 c.c.), is heated to boiling for five minutes in a sulphuric acid bath and the hydrochloric acid distilled off under diminished pressure. When the pale brown residue is dissolved in a small quantity of boiling water and stirred, crystallisation soon sets in, and the chloride separates in striated, hexagonal plates.

The ochreous mass is collected, dissolved in a little boiling water, and mixed with an equal volume of concentrated hydrochloric acid, when the chloride separates in characteristic balls of needles or plates, according to the concentration. The substance contains water of crystallisation, which was not determined, and, after drying at 70° and then over phosphoric oxide in a vacuum desiccator, the following analyses indicate that it still contains $1H_2O$:

0·1112 gave 0·2568 CO_2 and 0·0590 H_2O. C=63·0; H=5·9.
0·1118 „ 0·2562 CO_2 „ 0·0597 H_2O. C=62·5; H=5·9.
$C_{21}H_{22}O_4NCl,H_2O$ requires C=62·1; H=5·9 per cent.

ψ-Methylberberinium chloride softens at 80—82°, gradually shrinks, and becomes a syrup below 100°. It is readily soluble in warm water or methyl alcohol, but insoluble in ether, and when

ether is added to the solution in methyl alcohol, a milky liquid results, from which the chloride rapidly separates in highly characteristic stars of pale yellow needles. The solution of a trace of the chloride in a drop of acetic acid gives, on the addition of sulphuric acid, at first no coloration, but a salmon tint soon develops and rapidly changes to intense permanganate colour. A splinter of the chloride on a watch-glass, when moistened with concentrated nitric acid, dissolves to an intense crimson solution. The aqueous solution of the chloride is coloured yellow by ammonia, but gives no precipitate, and it behaves in the same way with cold sodium hydroxide, but when placed in the steam-bath the yellow solution becomes orange, then brown, and a dirty green base separates. The addition of methyl-alcoholic potassium hydroxide to the methyl-alcoholic solution of the chloride causes a separation of potassium chloride, but the yellowish-brown solution yields no precipitate with water. If the solution in dilute methyl-alcoholic potassium hydroxide is heated in the steam-bath, the liquid on the side of the test-tube dries to a brilliant crimson; after a time, this no longer occurs, and a black, amorphous precipitate separates which dissolves in hydrochloric acid to a brownish-pink solution. Even when mixed with powdered ice, the aqueous solution of the chloride instantly decolorises permanganate (984).

The *platinichloride*, $(C_{21}H_{22}O_4N)_2PtCl_6$, is a pale salmon coloured precipitate, and it is curious that when it is filtered off, the mother liquor is deep pink, exactly as was observed in the case of the preparation of the platinichloride from ψ-cryptopine chloride (985). When heated in a capillary tube, it loses its salmon colour at 200° and becomes yellow, then gradually darkens, shrinks together above 210°, and melts at about 243° with effervescence to a black tar:

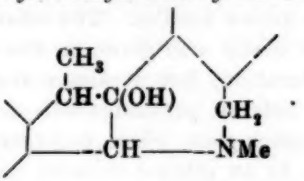
0·1216 gave 0·2026 CO_2 and 0·0435 H_2O. C = 45·4; H = 4·0.
0·2124 „ 0·0366 Pt. Pt = 17·2.
$(C_{21}H_{22}O_4N)_2PtCl_6$ requires C = 45·3; H = 4·0; Pt = 17·5 per cent.

ψ-Berberinium Iodide, $C_{21}H_{22}O_4NI$.—The hot dilute solution of the chloride gives, with potassium iodide, a clear solution which may not crystallise for days, but gradually deposits groups of almost colourless warts:

0·1072 gave 0·2068 CO_2 and 0·0471 H_2O. C = 52·6; H = 4·8.
$C_{21}H_{22}O_4NI$ requires C = 52·6; H = 4·6 per cent.

This iodide darkens at 160—165° and decomposes at 175—180° to a brown mass. It is very sparingly soluble in water, more readily so in boiling alcohol, from which it separates in microscopic groups of needles.

The Hydroxyisoanhydrodihydromethylberberines, (A) and (B).



These substances, which correspond with the hydroxy*iso*anhydrodihydrocryptopines, (*A*) and (*B*), result from the action of dilute hydrochloric acid on anhydromethylberberine. The base (2 grams) is mixed with concentrated hydrochloric acid (2·5 c.c.) and water (8 c.c.) in a test-tube, when the crystals, although they appear to change, do not dissolve, but pass rapidly into solution on warming with the formation of a yellow liquid. The test-tube is placed in boiling water, which causes the colour to deepen considerably, and after twenty minutes the tube is withdrawn, when, in a short time, the liquid clouds and a heavy syrup separates which, on keeping, becomes a hard button.

The product may be worked up in two different ways.

(i) The whole is dissolved in hot water, made strongly alkaline with ammonia, and the chalky precipitate immediately extracted with much ether, in which, in this condition, it is readily soluble. The ethereal solution is washed, rapidly dried over anhydrous potassium carbonate, and concentrated, during which, and while the solution is still boiling, a crystalline crust of prisms begins to separate, and increases very much on keeping.* If the ethereal solution is not too concentrated, this substance, after collecting and washing with ether, may melt at once at 208—210°, and consist of almost pure hydroxy*iso*anhydrodihydromethylberberine (*A*). If this is not the case, the substance is recrystallised from ether or from methyl alcohol.

The modification (*B*) of the hydroxy-compound is contained in

* In the description of hydroxy*iso*anhydrodihydrocryptopine (*A*) (996), it is stated that attempts to obtain this base in a crystalline condition were unsuccessful. This may, however, be accomplished by employing ether as the solvent. The hydrochloride (m. p. 227°) is dissolved in hot water, the solution cooled, and covered with much pure ether; on the addition of excess of ammonia and shaking, the base passes readily into solution. The ethereal solution is dried over potassium carbonate and concentrated, when, on remaining in a closed flask for some months in the ice-chest, nodular masses separate which melt at 177–180°. (Found, C=68·0; H=6·3. $C_{21}H_{23}O_4N$ requires C=68·3; H—6·2 per cent.) The nodules dissolve readily in boiling methyl alcohol or acetone and separate, on long keeping, in microscopic prisms.

the ethereal mother liquors, and is isolated in the manner described below.

(ii) A method of separation which allows of the modification (*A*) being rapidly obtained in a pure condition depends on the fact that this modification is much less readily soluble in cold methyl alcohol than the modification (*B*). The chalky precipitate, obtained as just described, is dried on porous porcelain, triturated with methyl alcohol, filtered, and the residue washed with methyl alcohol two or three times. After drying, the almost colourless mass melts at about 195—197°, and one recrystallisation from methyl alcohol is sufficient to raise the melting point to 210—212°, and the substance is then the pure modification (*A*). The methyl-alcoholic mother liquors are then mixed with water, the base extracted with ether, and the ethereal solution washed well, dried over potassium carbonate, and fractionally concentrated, when crops of crystals of varying composition are obtained, and these are comparatively easily separated into the pure modifications (*A*) and (*B*) by recrystallisation from methyl alcohol or ether.

Hydroxyisoanhydrodihydromethylberberine (*A*) is very sparingly soluble even in boiling methyl alcohol, separates in rather indefinite crusts, and melts at 210—212°. It is also sparingly soluble in boiling benzene, acetone, light petroleum, or ether, but dissolves somewhat in boiling methylal, and separates, on cooling, in warty groups:

0·1021 gave 0·2546 CO_2 and 0·0566 H_2O. C = 68·0; H = 6·2.
0·1135 „ 3·8 c.c. N_2 at 16° and 755 mm. N = 3·8.
$C_{21}H_{23}O_5N$ requires C = 68·3; H = 6·2; N = 3·8 per cent.

The base dissolves readily in dilute mineral acids, and as the solutions remain without crystallising, often for days, it was at first thought that the salts were very readily soluble. This is, however, not so, because in the case of the hydrochloride, for example, if a crystal of the hydrochloride (see below) is introduced into the warm, clear solution of the salt, a very sparingly soluble salt separates as a sandy, rather indefinitely crystalline powder. The characteristic behaviour of this base towards acids is well shown by rubbing a few crystals with dilute hydrochloric acid in a test-tube, when most dissolves, but some adheres to the sides as a gum. If the test-tube is placed in hot water, the gum immediately begins to crystallise, and, on stirring, the solution becomes filled with the hydrochloride, which is now remarkably sparingly soluble in boiling dilute hydrochloric acid. The base is readily soluble in acetic acid, and the addition of sulphuric acid produces a deep orange coloration.

Hydroxyisoanhydrodihydromethylberberine (*B*) separates from ethereal solution, on spontaneous concentration, in single, glistening prisms, very different in appearance from the hard crusts of the modification (*A*). It melts at 168—170°, and is generally more readily soluble than the modification (*A*). It is rather sparingly soluble in cold methyl alcohol, but readily so on warming, and separates on slow cooling in glistening prisms:

0·1032 gave 0·2589 CO_2 and 0·0580 H_2O. C = 68·4; H = 6·2.
$C_{21}H_{23}O_5N$ requires C = 68·3; H = 6·2 per cent.

This base does not show the behaviour with hydrochloric acid so characteristic of the modification (*A*). It is readily soluble in warm dilute hydrochloric acid, and, on cooling, the solution clouds and deposits a yellow syrup which gradually hardens, but shows little tendency to crystallise.

Action of Acetyl Chloride on the Hydroxyisoanhydrodihydromethylberberines, (A) and (B).

The modifications (*A*) and (*B*) of this hydroxy-derivative both yield the same products when they are subjected to the action of acetyl chloride at 100°. In each case, the base (1 gram) was sealed up with freshly distilled acetyl chloride (2 c.c.), when action took place at once with some evolution of heat, and a lemon-yellow, sandy precipitate separated. After the tube had been heated in boiling water for fifteen minutes, the excess of acetyl chloride was evaporated and the residue mixed with much cold water, which caused it to become pale green. On heating to boiling, the green colour disappeared, and a viscid precipitate (*C*) separated, which was collected and washed with warm water. This hydrochloride dissolves in boiling methyl alcohol, and, on cooling, rhombic plates gradually separate of angle 78° which are strongly doubly refracting and show straight extinction:

0·1073 gave 0·2415 CO_2 and 0·0562 H_2O. C = 61·4; H = 5·8.
$C_{23}H_{25}O_6N,HCl$ requires C = 61·6; H = 5·8 per cent.

This hydrochloride melts at about 253° with vigorous decomposition to a reddish-brown froth. It dissolves in much boiling water, but is remarkably sparingly soluble in boiling dilute hydrochloric acid, and separates in groups of thin laminæ with arrow-shaped ends. The hot aqueous solution yields, on the addition of ammonia, a milky liquid which soon begins to deposit colourless, crystalline flakes, and after these had been collected and washed and left to dry on porous porcelain, they were found to melt in the steam-oven and to solidify, on cooling, to a colourless resin. In contact with methyl alcohol, this resin at once became crystal-

line, dissolved on boiling, and well-developed, flat prisms separated, on keeping, which melted sharply at 166—167°:

0·1059 gave 0·2611 CO_2 and 0·0595 H_2O. C = 67·1; H = 6 2.

$C_{23}H_{25}O_6N$ requires C = 67·2; H = 6·1 per cent.

The methyl-alcoholic mother liquors, when left exposed to the air, deposited warty masses which melted at 208—210°, and consisted of hydroxy*iso*anhydrodihydromethylberberine (*A*), and it would therefore seem that the substance melting at 165—167° is the acetyl derivative of this modification (*A*). This is confirmed by the fact that this acetyl base yields, on treatment with hydrochloric acid, a very sparingly soluble hydrochloride which separates from methyl alcohol in rhombs with the angle 78°, and melts and decomposes at 253°.

The mother liquors and washings of the hydrochloride (*C*, see above) gave with ammonia a chalky precipitate, which was collected and crystallised from methyl alcohol, in which it was sparingly soluble, and from which it separated in crusts of nodules melting at 213—215° (*D*):

0·1061 gave 0·2638 CO_2 and 0·0593 H_2O. C = 67·8; H = 6·2.

$C_{23}H_{25}O_6N$ requires C = 67·2; H = 6·1 per cent.

This substance is presumably the acetyl derivative of hydroxy-*iso*anhydrodihydromethylberberine (*B*). When it was mixed with warm dilute hydrochloric acid, it was converted into the hydrochloride, which separated from methyl alcohol in oblique, rhombic plates with an angle of 70°. After drying in the steam-oven until constant in weight, this salt yielded the following analysis:

0·1189 gave 0·2716 CO_2 and 0·0650 H_2O. C = 62·3; H = 6·0.

$C_{23}H_{25}O_6N$,HCl requires C = 61·6; H = 5·8 per cent.

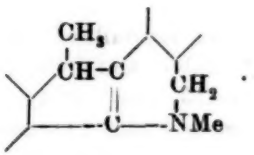
This hydrochloride darkens above 220° and decomposes at 230° with vigorous effervescence to an orange syrup. It dissolves readily in hot water and separates in a very characteristic manner, namely, in very thin, perfectly formed, nearly square plates with bevelled edges.

The mother liquors from this hydrochloride deposit, on concentration, rhombic prisms of angle 78°, which melt at 253—255° with vigorous effervescence, and evidently consist of the hydrochloride (*C*), partial molecular change having taken place during the conversion of the acetyl base (*D*) into the hydrochloride. That intramolecular changes of this nature take place readily under a variety of conditions is evidenced by the two following experiments, which were made with the object of determining whether it was possible to obtain base (*B*) from the acetyl derivative (*D*) by hydrolysis, and thus to confirm the relationship of these substances.

(i) The acetyl derivative (*D*) was boiled with dilute sulphuric acid (20 per cent.) for ten minutes, ammonia was then added, and the base crystallised from methyl alcohol, from which it separated as a rather indefinite, crystalline crust melting at 209—211°, and consisting of hydroxy*iso*anhydrodihydroberberine (*A*). The methyl-alcoholic mother liquors deposited, on slow evaporation in the ice-chest, groups of needles which melted at 165—168°, and proved to be the modification (*B*) of the same hydroxy-base.

(ii) The acetyl derivative (*D*) was boiled with 10 per cent. methyl-alcoholic potassium hydroxide until it had dissolved and the solution concentrated, when, on keeping in the ice-chest, a crystalline substance separated which melted at 208—210°, and consisted of modification (*A*) of the hydroxy-derivative.

iso*Anhydromethylberberine*,



The hydrochloride of this base may be obtained from either of the hydroxy*iso*anhydrodihydromethylberberines, (*A*) or (*B*), by boiling with concentrated hydrochloric acid or, better, by digesting with phosphoryl chloride. The following two experiments will illustrate this conversion.

(i) Hydroxy*iso*anhydrodihydromethylberberine (*B*, 2 grams) was boiled with concentrated hydrochloric acid (20 c.c.) for half an hour by means of a sulphuric acid bath, during which a sparingly soluble hydrochloride separated as a crust on the sides of the test-tube. The hydrochloric acid was distilled off under diminished pressure, the pale ochreous residue dissolved in much boiling water, the solution concentrated, and left in the ice-chest, when a considerable crop of the hydrochloride of *iso*anhydromethylberberine gradually separated.

(ii) Hydroxy*iso*anhydrodihydromethylberberine (*A*, 2 grams) was mixed with freshly distilled phosphoryl chloride (6 c.c.), in which it did not dissolve in the cold, but, on warming, solution took place readily with the evolution of sufficient heat to raise the temperature from 60° to the boiling point. After boiling for ten minutes, the excess of oxychloride was distilled off under 15 mm. pressure, and the deep yellow gum dissolved in much boiling water, when, on concentration and vigorous stirring, a large crop of the sparingly soluble hydrochloride of *iso*anhydromethylberberine separated.

The hydrochloride from either (i) or (ii) was recrystallised from much hot water, dissolved in boiling water, and mixed with ammonia, when a milky liquid resulted which soon crystallised, and the base was further purified by crystallisation from methyl alcohol:

0·1011 gave 0·2655 CO_2 and 0·0545 H_2O. C = 71·6; H = 6·0.
$C_{21}H_{21}O_4N$ requires C = 71·8; H = 6·0 per cent.

iso*Anhydromethylberberine* melts at 123—124° and is readily soluble in methyl alcohol, separating in glistening prisms, which, however, were not suitable for measurement and comparison with the crystals of *iso*anhydrocryptopine (1003). It is very readily soluble in benzene, but rather sparingly so in light petroleum; it may, however, be crystallised from light petroleum (b. p. 80—90°), from which it separates in groups of needles like fern fronds. It is very readily soluble in ether, and crystallises well from this solvent. It dissolves readily in acetic acid, and the addition of sulphuric acid produces a deep orange colour, which becomes brown on adding a drop of dilute nitric acid. When the base is heated in a test-tube, there is much charring and the development of a strong odour of dimethylamine.

The Hydrochloride, $C_{21}H_{21}O_4N,HCl$.—This salt is sparingly soluble in water, and particularly so in dilute hydrochloric acid, and separates in brilliant, elongated prisms which are somewhat curved. It crystallises from methyl alcohol in brilliant, prismatic tablets with many facets, and melts at about 205—210° with previous softening.

The air-dried salt lost 3·7 per cent. at 100°, and gave the following results:

0·1066 gave 0·2538 CO_2 and 0·0556 H_2O. C = 64·9; H = 5·8.
$C_{21}H_{21}O_4N,HCl$ requires C = 64·9; H = 5·7 per cent.

The Hydriodide.—A boiling dilute aqueous solution of the hydrochloride gives no precipitate on adding boiling dilute potassium iodide, but, on keeping, the iodide soon commences to separate in indefinite, nodular groups:

0·1092 gave 0·2113 CO_2 and 0·0455 H_2O. C = 52·7; H = 4·6.
$C_{21}H_{21}O_4N,HI$ requires C = 52·6; H = 4·6 per cent.

When quickly heated, this hydriodide does not discolour until about 215°, and decomposes at about 247° to a nearly black froth. It is almost insoluble in cold water and sparingly so in cold alcohol, but it dissolves comparatively readily in boiling alcohol and separates in two distinct forms, namely, in stars or groups of needles or in short, brilliant prisms. When the solution is warmed,

the needles dissolve and leave the prisms, and it is evident, therefore, that this salt is dimorphic.

Action of Dilute Sulphuric Acid on iso*Anhydromethylberberine.*

The sulphate of *iso*anhydromethylberberine is readily soluble, and if the solution in a large excess of dilute sulphuric acid is boiled for half an hour and then made alkaline with ammonia, an amorphous base separates, which may be extracted with ether. The ethereal solution was thoroughly washed, dried over potassium carbonate, and concentrated, when, on remaining in the ice-chest for several days, a crust of needles formed, but in comparatively small amount. The substance was collected, washed with ether, in which it was sparingly soluble, and crystallised from methyl alcohol, in which the base is remarkably sparingly soluble, and from which it separated as a crystalline crust.

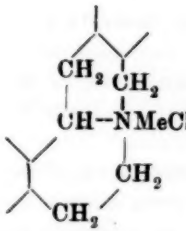
It melted at 212—215°, and consisted of hydroxy*iso*anhydrodihydromethylberberine (*A*). (Found: C = 68·4; H = 6·1. $C_{21}H_{23}O_5N$ requires C = 68·3; H = 6·2 per cent.) The ethereal mother liquor from the crystallisation of this modification yielded, on concentration, a small quantity of the modification (*B*) melting at 165—167° (compare p. 732).

Reduction of Dihydroanhydroberberine Methochloride.

In studying this reduction, the methochloride (30 grams), dissolved in hot water (1 litre), was mixed with concentrated hydrochloric acid (50 c.c.) and heated to boiling in an enamelled basin. Sodium amalgam (1500 grams of 3 per cent.) was then added, in three portions, together with sufficient hydrochloric acid to keep the liquid strongly acid. The product, separated from the mercury, clouded on cooling, and when mixed with excess of ammonia deposited a viscid, pale brown precipitate which, on keeping, soon hardened. This was collected, washed with a little warm water, dried on porous porcelain, and extracted with ether (*X*), which left a nearly colourless mass undissolved.

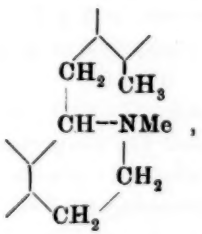
The latter was found to consist of a quaternary chloride, and a further considerable quantity of the same substance was obtained from the washings of the precipitate which had separated on the addition of ammonia. The whole was repeatedly crystallised from hot dilute hydrochloric acid, and thus separated into two quaternary chlorides, (*α*) and (*β*), melting approximately at 245—250° and 280—285° respectively. The chloride (*α*) is, after drying at 100°, anhydrous, and has the formula $C_{21}H_{24}O_4NCl$. (Found: C = 64·5; H = 6·3. Calc.: C = 64·7; H = 6·2 per cent.) The chloride (*β*),

melting at 280—285°, retains $1H_2O$ after drying at 100°. (Found: C = 61·7; H = 6·3. $C_{21}H_{24}O_4NCl,H_2O$ requires C = 61·8; H = 6·4 per cent.) There can be no doubt that these substances are the α- and β-methochlorides of tetrahydroanhydroberberine (compare p. 733),



first described by Pyman (T., 1913, **103**, 825, 826), and this was confirmed by the fact that the β-chloride, on digesting with methyl-alcoholic potassium hydroxide, yielded a base which separated from methyl alcohol in colourless nodules, melted at 108—110°, and consisted of methyl*iso*tetrahydroanhydroberberine (base *B*), which Pyman obtained by the dehydration of tetrahydroanhydroberberine methohydroxide (*loc. cit.*, p. 827). The identity was confirmed by analysis. (Found: C = 71·2; H = 6·6. $C_{21}H_{23}O_4N$ requires C = 71·4; H = 6·5 per cent.)

The ethereal extract (*X*) from the crude quaternary chlorides (see above) was thoroughly washed with water, dried over potassium carbonate, and evaporated, when a syrup was obtained which, even on long keeping in the ice-chest and frequent stirring, showed no signs of crystallising. That this substance is *dihydromethyliso-tetrahydroanhydroberberine* (p. 733),



is indicated by its properties, and an analysis supported this view and suggested that the base was nearly pure:

0·1046 gave 0·2730 CO_2 and 0·0672 H_2O. C = 71·3; H = 7·1.

$C_{21}H_{25}O_4N$ requires C = 71·0; H = 7·0 per cent.

The salts are readily soluble and exhibit little tendency to crystallise. The *platinichloride* was prepared by adding platinic

chloride to a dilute solution of the hydrochloride, and is a chalky, salmon coloured precipitate:

0·1021 gave 0·1703 CO_2 and 0·0437 H_2O. C=45·5; H=4·7.

0·4764 „ 0·0802 Pt. Pt=16·9.

$(C_{21}H_{25}O_4N)_2H_2PtCl_6$ requires C=45·0; H=4·7; Pt=17·4 per cent.

The Methosulphate.—This derivative was prepared by adding methyl sulphate (3 c.c.) to the solution of the base (3 grams) in warm benzene (15 c.c.), when a rise of temperature was observed, but there was no separation even after keeping for three days in the ice-chest.

On the addition of dry ether, the methosulphate was precipitated as a syrup, and was washed with ether, dissolved in a little methyl alcohol, and boiled with a considerable excess of methyl-alcoholic potassium hydroxide for fifteen minutes under such conditions that most of the methyl alcohol distilled away. Water was added, the caseous precipitate extracted with much ether, the ethereal solution thoroughly washed, dried over potassium carbonate, and evaporated, when a syrup remained which, on keeping, gradually crystallised to a striated mass of needles.

This was dissolved in dilute hydrochloric acid, the solution filtered, made alkaline with ammonia, and again extracted with ether, the ethereal solution being dried over potassium carbonate and evaporated, when the syrup again crystallised. After remaining in contact with porous porcelain over phosphoric oxide for several days, the following results were obtained on analysis:

0·1112 gave 0·2894 CO_2 and 0·0735 H_2O. C=71·0; H=7·3.

$C_{22}H_{27}O_4N$ requires C=71·5; H=7·3 per cent.

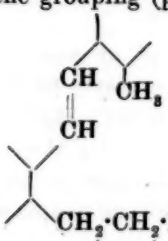
This base is very readily soluble in the usual solvents, and all attempts to recrystallise it were unsuccessful. The *platinichloride*, prepared in the usual manner, is a pale ochreous precipitate:

0·1017 gave 0·1731 CO_2 and 0·0449 H_2O. C=46·4; H=4·9.

0·4759 „ 0·0798 Pt. Pt=17·0.

$(C_{22}H_{27}O_4N)_2H_2PtCl_6$ requires C=46·0; H=4·9; Pt=16·9 per cent.

The analytical results and the properties of this base leave little doubt that it is *dihydrodimethylisotetrahydroanhydroberberine* (950), and contains the grouping (p. 734)



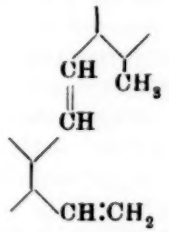
The *methosulphate* was prepared by dissolving the base (5 grams) in benzene and adding methyl sulphate (5 c.c.), when there was a considerable rise of temperature, and a syrup separated which soon commenced to crystallise and, on remaining in the ice-chest, became a soft mass of glistening needles. The crystals were collected, washed with benzene, transferred to porous porcelain, dried, and analysed:

0·1182 gave 0·2506 CO_2 and 0·0701 H_2O. C=57·8; H=6·6.

$C_{22}H_{27}O_4N,Me_2SO_4$ requires C=58·2; H=6·6 per cent.

This methosulphate is readily soluble in water or methyl alcohol and difficult to recrystallise, but it separates, when its solution in water is allowed to concentrate over sulphuric acid, as a soft mass of needles.

Berberidene,



In preparing this interesting substance, the methosulphate of dihydrodimethyl*iso*tetrahydroanhydroberberine was digested on the steam-bath with a large excess of methyl-alcoholic potassium hydroxide (20 per cent.), when decomposition readily set in with the elimination of trimethylamine. After twenty minutes, most of the methyl alcohol was distilled off, water was added, and the caseous precipitate extracted with much ether, in which in this condition it is moderately readily soluble. The ethereal solution was very thoroughly washed, dried over potassium carbonate, and concentrated, when, on keeping, the new substance separated as a crust of brilliant prisms:

0·1115 gave 0·3029 CO_2 and 0·0625 H_2O. C=74·1; H=6·2.

0·1062 „ 0·2877 CO_2 „ 0·0592 H_2O. C=73·9; H=6·2.

$C_{20}H_{20}O_4$ requires C=74·1; H=6·2 per cent.

Berberidene melts at 113—114°, and is characterised by the facility with which it crystallises. It is very sparingly soluble even in boiling methyl alcohol, and separates as a voluminous, glistening mass of irregular laminæ which, when free from any yellow mother liquor, have a most striking lilac fluorescence. It is readily soluble in benzene, but sparingly so in light petroleum, from which it separates in groups of needles. It is sparingly soluble in acetic acid in the cold, but dissolves readily on boiling,

and separates in rhombs or in brilliant, stout prisms with an oblique termination; if, however, the separation takes place rapidly, the crystallisation may be indefinite. Berberidene exhibits a very striking difference in its behaviour with methyl and ethyl alcohols. Whilst it is very sparingly soluble in methyl alcohol and crystallises well from this solvent, it dissolves quite readily in ethyl alcohol and separates only from quite concentrated solutions, and then as an indefinite crust composed of warts.

Oxidation of Berberidene.

In studying this oxidation (p. 735), finely sieved permanganate (4 grams) was gradually added, at the ordinary temperature, to the pure substance (2·3 grams) dissolved in acetone (60 c.c.), when oxidation took place readily with distinct rise of temperature, but care was taken that this did not exceed 18°. The product was filtered, the manganese precipitate thoroughly washed with acetone (*A*), and repeatedly extracted with small quantities of boiling water. The brown, aqueous extract was considerably concentrated and acidified with hydrochloric acid, when a viscid, brown acid separated which proved difficult to purify, but ultimately the following process was successful: The brown mass (about 1 gram) was boiled with water (200 c.c.) and filtered from the dark brown tar; the latter was warmed with dilute ammonia, when nearly all dissolved, and, after boiling with animal charcoal and filtering, the acid was again precipitated and boiled with water (100 c.c.). The combined aqueous extracts were neutralised with sodium carbonate, mixed with a little animal charcoal, evaporated to about 20 c.c., and filtered.

The nearly colourless filtrate gave, on acidifying, a chalky precipitate which melted at about 174°, and separated from glacial acetic acid as a satiny mass of plates. (Found: C = 61·0; H = 6·1. $C_{10}H_{12}O_4$ requires C = 61·2; H = 6·1 per cent.)

The pure acid melted at 183—184°, and was found by direct comparison to be identical with 5:6-*dimethoxy-o-toluic acid*, $C_6H_2Me(OMe)_2{\cdot}CO_2H$, which had been previously obtained (921) by the methylation of 5:6-dihydroxy-*o*-toluic acid. The melting point is there given as 177°, but repeated recrystallisation from glacial acetic acid raises this to 184°.

The mother liquors from the purification of the 5:6-dimethoxy-*o*-toluic acid were concentrated under diminished pressure until nearly dry, mixed with sand, and extracted with ether in a Soxhlet apparatus. The ethereal solution yielded, on evaporation, a small, crystalline residue which was separated by crystallisation from hydrochloric acid into 5:6-dimethoxy-*o*-toluic acid, and a more

readily soluble acid which separated from a little water in six-sided plates melting at about 171—174°, and, on heating, yielded an anhydride melting at about 170—173°. Since this acid gave a negative result for methoxy-groups in the Zeisel apparatus, there can be little doubt that it was hydrastic acid, $CH_2{:}O_2{:}C_6H_2(CO_2H)_2$, but the quantity was insufficient for analysis. The acetone extract (*A*) of the manganese precipitate yielded, on evaporation, a syrup (1·2 grams) which gradually crystallised in nodular masses. When this was submitted to distillation in a current of steam, a cloudy distillate was obtained in which oily drops were visible. The whole was extracted with pure ether, the ethereal solution washed, dried over potassium carbonate, and evaporated, when a colourless oil remained which rapidly crystallised in long needles. The crystals were left in contact with porous porcelain until quite dry, melted, and, after again crystallising, transferred once more to porous porcelain. Finally, the substance was dried over phosphoric oxide in a vacuum desiccator and analysed. (Found: C = 66·5; H = 6·8. $C_{10}H_{12}O_3$ requires C = 66·7; H = 6·7 per cent.)

This substance was 5 : 6-dimethoxy-*o*-tolualdehyde,

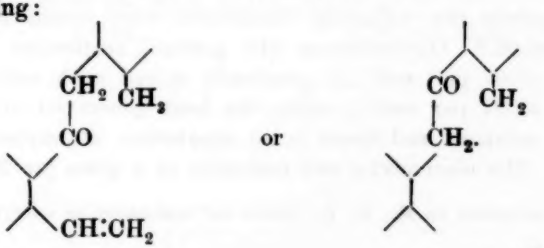
$$C_6H_2Me(OMe)_2{\cdot}CHO,$$

since it melted at 52—53°, and, when mixed with a specimen of this aldehyde which had previously been obtained by the methylation of 5-methoxy-*o*-tolualdehyde (915), there was no alteration in melting point.

The residue in the steam distillation flask contained a viscid oil, which was extracted with ether, the ethereal solution washed well, dried over potassium carbonate, and evaporated, when a pale yellow syrup remained, which soon began to crystallise in nodules and ultimately became solid. The mass was triturated with methyl alcohol, which removed oily impurity, transferred to porous porcelain, and recrystallised from glacial acetic acid:

0·1265 gave 0·3285 CO_2 and 0·0679 H_2O. C = 70 8; H = 6·1.
$C_{20}H_{20}O_5$ requires C = 70·6; H = 5·9 per cent.

Since this substance yields a semicarbazone (see below), there can be little doubt that it is *ketodihydroberberidene* and contains the grouping:



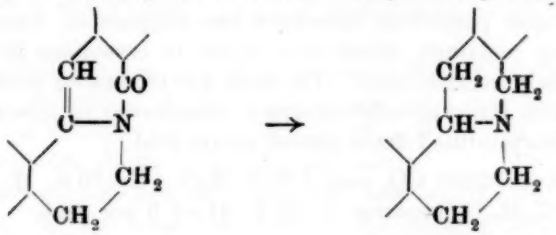
It is rather sparingly soluble in cold glacial acetic acid, much more readily so on boiling, and separates well in very pale yellow stars made up of elongated, rhombic plates. It melts at 118—120° and is remarkably sparingly soluble even in boiling methyl alcohol, from which it crystallises as a pale lemon-yellow powder consisting of small, glistening prisms. The crystals are coloured crimson by concentrated nitric acid, partly dissolve, and the addition of water gives an ochreous precipitate. When sulphuric acid is added to the solution of a trace of the substance in glacial acetic acid, a brown coloration is obtained, which is intensified by the addition of a drop of dilute nitric acid.

The *semicarbazone*, $C_{21}H_{23}O_5N_3$, was prepared by boiling the substance with much alcohol and excess of semicarbazide hydrochloride and sodium acetate, when solution took place readily, and, on evaporation to dryness, a crystalline mass remained. This was triturated with water, collected, washed well, and crystallised from methyl alcohol:

0·1027 gave 0·2376 CO_2 and 0·0570 H_2O. C = 63·1; H = 6·1.
0·1239 „ 9·7 c.c. N_2 at 17° and 752 mm. N = 10·6.
$C_{21}H_{23}O_5N_3$ requires C = 63·5; H = 5·8; N = 10·6 per cent.

This *semicarbazone* melts and effervesces at about 218—220° and is sparingly soluble in boiling methyl alcohol, from which it separates in nodular masses.

Reduction of Oxyberberine to Tetrahydroanhydroberberine,



The main difficulty in carrying out this reduction is the sparing solubility of oxyberberine in dilute acids or in organic solvents, but ultimately the following conditions were found to give the desired result.* Oxyberberine (10 grams), suspended in alcohol (260 c.c. of 97 per cent.), is gradually mixed with sulphuric acid (130 c.c. of 97 per cent.), when the heat generated brings about complete solution and there is no separation of oxyberberine on keeping. The electrolytic cell consisted of a glass jar 20 cm. high

* I am indebted to Mr. G. R. Clemo for assistance in carrying out this reduction.

and of 1 litre capacity; the cathode was a sheet of lead which just fitted round the inside of the glass jar, and, previous to the experiment, had been coated with a layer of electrolytic lead. The anode was a strip of lead, and this was placed in a porous cell, 5 cm. in diameter, containing dilute sulphuric acid (20 per cent.), which was replenished from time to time during the experiment. In carrying out the reduction, the solution, prepared as described above, was placed in the cathodic compartment and a current of about 6 amperes passed for forty-eight hours. The pale yellow product was mixed with ice and water (about 500 grams), allowed to remain for twenty-four hours, and then filtered. The rather considerable grey precipitate (5·3 grams) is largely soluble in hot glacial acetic acid, and, after filtering, the solution deposits oxyberberine acetate (1·5 grams). The portion insoluble in acetic acid (0·8 gram) melts above 300°, and was not further examined. The filtrate from the grey precipitate gives with excess of ammonia a dark-coloured precipitate (4·6 grams), which is collected, dried, and digested with a little methyl alcohol, when much of the dark impurity dissolves and a much cleaner product is left. This is dissolved in boiling, very dilute hydrochloric acid with the addition of animal charcoal and concentrated, when, on keeping, a deep ochreous, crystalline precipitate separates in quantity. The hydrochloride is collected, recrystallised from boiling glacial acetic acid, and the colourless salt decomposed by ammonia. Finally, the base is twice crystallised from acetone, from which it separates in colourless, glistening leaflets. (Found: C = 70·6; H = 6·2. $C_{20}H_{21}O_4N$ requires C = 70·8; H = 6·2 per cent.)

This substance melted at 170—171°, and a careful examination both of the base and of its salts clearly established the identity with tetrahydroanhydroberberine (m. p. 170—171°). Moreover, a mixture of the substance with tetrahydroanhydroberberine melted at 170—171°.

The author is much indebted to Mr. Fred Hall for carrying out the analyses given in this paper.

THE UNIVERSITY CHEMICAL LABORATORIES,
OXFORD. [*Received, August 17th*, 1918.]

LXVI.—*Morindone.*

By John Lionel Simonsen.

During the past few years, owing to the shortage of synthetic dyes, the use of natural colouring matters has, to some extent, been revived, and it appeared, therefore, to be a matter of some interest to attempt to elucidate the constitution of the main constituent of *Morinda citrifolia* and *M. umbellata*, morindone, since the root bark of this tree at one time found considerable application in India for the dyeing of cloth.

Morindone occurs in the root bark mainly in the form of the glucoside, morindin, although a small quantity of the free colouring matter is present in the bark. Morindin appears to have been first isolated from *M. citrifolia* by Anderson (*Annalen*, 1849, **71**, 216). He ascribed to it the formula $C_{28}H_{30}O_{15}$, and by sublimation obtained a substance resembling alizarin in its properties, to which he gave the name morindone. Subsequent investigators appear to have regarded morindin as identical with ruberythric acid and morindone as identical with alizarin. Thorpe and Greenall (T., 1887, **51**, 52), and later Thorpe and Smith (T., 1888, **53**, 171), using *M. citrifolia* as the source of their material, proved conclusively, however, that morindone possessed the formula $C_{15}H_{10}O_5$, and were of the opinion that morindin was more correctly represented by the formula $C_{26}H_{28}O_{14}$ than by the formula suggested by Anderson. They further considered morindone to be a trihydroxymethylanthraquinone.

The presence of morindin and morindone in *M. umbellata* was first proved by Perkin and Hummel (T., 1894, **65**, 851) in their investigation of the constituents of the root bark of this tree. They confirmed the formula $C_{26}H_{28}O_{14}$ (with eight hydroxy-groups) for morindin, and they further showed that in all probability morindone was a trihydroxymethylanthraquinone derived from 2-methylanthraquinone, since, when distilled with zinc dust, 2-methylanthracene was obtained.

Subsequently, Oesterle and Tisza (*Arch. Pharm.*, 1907, **245**, 534) investigated once more the constituents of *M. citrifolia*. They drew the conclusion that morindin from that source had the formula $C_{27}H_{30}O_{15}$ and contained nine hydroxy-groups. They based this conclusion on an analysis of morindin, its acetyl and benzoyl derivatives, and on a quantitative determination of the products of hydrolysis. The properties of the morindin obtained by these authors, and also those of its derivatives, are at distinct

variance with those described by Perkin and Hummel (*loc. cit.*). Perkin (P., 1908, **24**, 150) directed attention to these discrepancies and published further analyses in support of his formula for morindin from *M. umbellata*, and suggested that the morindin derived from *M. umbellata* and *M. citrifolia* might be different.

With regard to the constitution of morindone, beyond the fact that it possesses the formula $C_{15}H_{10}O_5$, contains three hydroxy-groups, and yields 2-methylanthracene on distillation with zinc dust, little is known. Perkin (Thorpe's "Dictionary of Applied Chemistry," III, 547) has suggested either that morindone might be a methylanthragallol or that it might contain a $\cdot CH_2 \cdot OH$ group, the presence of such a group having been suggested by Robinson and Simonsen (T., 1909, **95**, 1088) to explain the relationship between aloe-emodin and rhein, since, as he pointed out, the colour reactions of morindone are somewhat remarkable.

For the preparation of the morindin and morindone required for the experiments described in this paper, the author has used the root bark of *M. citrifolia*, which was obtained for him by Dr. J. R. Henderson, of the Madras Museum, and Mr. Y. Narasihman, lecturer in chemistry, Maharaja's College, Vizianagram, and a considerable quantity of the bark was very kindly extracted for him by Drs. Fowler and Watson at the Indian Institute of Science, Bangalore. The author wishes to take this opportunity of expressing his thanks to these gentlemen.

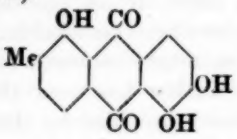
The morindin was extracted and purified essentially by the methods used by Perkin and Hummel, and it is not necessary to describe them in detail. In view of the discrepancies between the work of Perkin and Hummel and that of Oesterle and Tisza mentioned above, a specimen of morindin was very carefully purified by repeated crystallisation from 75 per cent. alcohol, when it was obtained in voluminous, yellow needles which, when rapidly heated, melted at 250—251°; when slowly heated, it sintered at 235° and melted at 245°. (Oesterle and Tisza state that it commenced to sublime at 235° and melted at 245°. Perkin and Hummel do not give a melting point.) The analytical data agreed well with the formula $C_{26}H_{28}O_{14}$ suggested by Perkin. The acetyl derivative was also prepared, and was found to melt at 239—240°. (Oesterle and Tisza give 236°, Perkin 246—248°.) As stated by Perkin, it is very sparingly soluble in cold alcohol, somewhat more readily so in the hot solvent, and contains eight acetyl groups. There would therefore appear to be no difference between the morindin derived from *M. citrifolia* and *M. umbellata*, and the discrepancies between the results of Perkin and Hummel and those of Oesterle and Tisza must be ascribed to some other cause. The author had

hoped to make a direct comparison of the morindins obtained from these two sources, but up to the present he has not succeeded in obtaining a specimen of the root bark of *M. umbellata*.

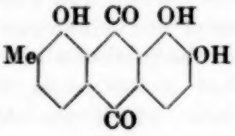
Attempts to isolate in a pure state the sugar formed by the hydrolysis of morindin were unsuccessful. The phenylosazone was prepared, but was found to be a mixture.

The Constitution of Morindone.

From a consideration of the experiments described in this paper and from the results obtained by previous investigators, the author would suggest that morindone is best represented either as a hydroxymethylanthrarufin (I) or as a hydroxymethylchrysazin (II).



(I.)



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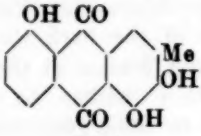

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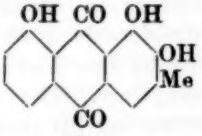


(IV.)

The evidence in support of this view may, perhaps, best be summarised as follows:

(i) The methyl group is in position 2, since morindone on distillation with zinc dust yielded 2-methylanthracene (Perkin and Hummel, *loc. cit.*, p. 856).

(ii) Morindone contains three hydroxy-groups, since it yields triacetyl, tribenzoyl, and trimethoxy-derivatives.

(iii) Two of the hydroxy-groups must be in the ortho-position with respect to the carbonyl groups of the anthraquinone nucleus, since treatment with methyl iodide and alkali only yielded a monomethyl ether (see p. 773).

(iv) Morindone is a mordant dye resembling alizarin, and hence probably has two of the hydroxy-groups in the 1:2-position.

(v) The hydroxy-group, which undergoes methylation with methyl iodide, must be present in the same ring as another hydroxy-group, since *morindone monomethyl ether* is completely destroyed when oxidised with an alkaline solution of potassium permanganate, only oxalic acid being isolated from the products (see p. 773).

(vi) Morindone cannot be a derivative of anthragallol or purpurin, since it is perfectly stable in alkaline solution and does not undergo oxidation even when air is drawn through such a solution for several days.

(vii) The presence of a $\cdot CH_2 \cdot OH$ group, as suggested by Perkin, is unlikely, since all attempts to detect such an alcoholic grouping by oxidation or displacement of the hydroxy-group by a halogen were unsuccessful.

From the above, it follows that the only positions for the hydroxy-groups are as in 1:5:6-trihydroxyanthraquinone or 1:7:8-trihydroxyanthraquinone.

(viii) It is suggested that the methyl group must be in the ortho-position with respect to one of the hydroxy-groups, since all attempts to oxidise it to a carboxyl group by means of chromic acid have proved unsuccessful, the molecule being completely destroyed when once attacked by the oxidising agent. As is well known, *o*-xylene cannot be oxidised to phthalic acid by means of chromic acid, and the author has further found that whereas *p*-tolyl methyl ether when oxidised by means of chromic acid in acetic acid solution gave an excellent yield of anisic acid, *o*-tolyl methyl ether under similar conditions did not yield a trace of the corresponding *o*-methoxy-acid.

(ix) If the view be accepted that the methyl group is in the ortho-position with respect to one of the hydroxy-groups, then four formulæ derived from hydroxyanthrarufin or hydroxychrysazin become possible (I, II, III, and IV). The author would reject formulæ III and IV, since it is highly improbable that substances possessing these formulæ would be methylated by methyl iodide, owing to steric hindrance.

(x) In deciding between formulæ I and II, it would appear that formula I is the more probable, since in its colour reactions morindone resembles more closely hydroxyanthrarufin than hydroxychrysazin. Hydroxyanthrarufin dissolves in sulphuric acid with a violet colour which, on the addition of boric acid, becomes blue; morindone dissolves in sulphuric acid with a blue colour, which is not changed on the addition of boric acid; moreover, the sulphuric–boric acid solutions of hydroxyanthrarufin and morindone are practically indistinguishable in colour. Hydroxychrysazin, on the other hand, dissolves in sulphuric acid with a red colour, which becomes purple on the addition of boric acid. The bluer shades exhibited by morindone are explained by the presence of the methyl group, since, as is well known, methylalizarin yields bluer shades than does alizarin.

Many experiments were made with the object of confirming the

formula suggested above for morindone, but up to the present without success. Morindone trimethyl ether was found to be extremely resistant to oxidising agents. It was only slowly attacked by an alkaline solution of potassium permanganate even in boiling solution. Experiments involving the use of either chromic acid or nitric acid gave only negative results.

The synthesis of morindone is being attempted, but the problem seems to be a difficult one.

Experimental.

Morindin.

The material, isolated and crystallised as described on p. 767 (Found: C = 55·3; H = 4·9. $C_{26}H_{28}O_{14}$ requires C = 55·3; H = 4·9 per cent.), was hydrolysed with an alcoholic solution of sulphuric acid, when 0·7556 gave 0·3632 morindone. Yield of morindone = 48·1 per cent., whereas if the formula for morindin were $C_{26}H_{28}O_{14}$, the yield of morindone should be 48·0 per cent.

Acetylmorindin.—This substance was readily prepared by boiling morindin with acetic anhydride containing a trace of pyridine for two hours. It separated from dilute acetic acid in pale sulphur-yellow needles, which melted at 239—240°. For analysis it was dried at 120° (Found: C = 56·1; H = 5·1. $C_{42}H_{44}O_{22}$ requires C = 56·0; H = 4·9 per cent.). The number of acetyl groups present was determined by A. G. Perkin's method, and was found to be eight. 0·2074 gave 0·1103 $C_2H_4O_2$, whence Ac = 38·2, whereas this amount of a substance of the formula $C_{26}H_{20}O_{14}(Ac)_8$ should yield 0·1106 $C_2H_4O_2$, Ac = 38·2 per cent.*

Morindone.

The morindone required for these experiments was obtained from morindin by hydrolysis with an alcoholic solution of sulphuric acid. After crystallisation from toluene, it melted at 275°, and showed all the properties ascribed to this substance (Found: C = 66·4; H = 3·7. Calc.: C = 66·7; H = 3·7 per cent.). Morindone was not attacked when heated with an acetic acid solution of hydrogen bromide (saturated at 0°) for some hours at 100° in a sealed tube, nor was it found to be altered when air was drawn through an alkaline solution for some days.

Acetylmorindone.—Acetylmorindone was prepared by heating morindone for two hours with acetic anhydride and anhydrous

* Oesterle and Tisza's formula $C_{27}H_{21}O_{13}(Ac)_9$ requires Ac = 39·8 per cent.

sodium acetate. It was purified by crystallisation from acetic acid, when it was obtained in pale yellow needles melting at 249° and commencing to sinter slightly at 243°. This melting point is considerably higher than that given by Perkin and Hummel (*loc. cit.*, p. 856), who state that acetylmorindone melts at 222°. I am, however, informed by Prof. Perkin that this value for the melting point is probably due to a misprint.

For analysis, a specimen was dried at 120°:

0·1129 gave 0·2645 CO_2 and 0·0427 H_2O. C = 63·8; H = 4·2.

$C_{21}H_{16}O_8$ requires C = 63·6; H = 4·0 per cent.

Acetylmorindone was not readily attacked by chromic acid, and all attempts to oxidise the methyl group by this reagent were unsuccessful. Thus, when treated with the quantity of chromic acid calculated to oxidise the methyl group to a carboxyl group, a portion of the substance appeared to undergo complete destruction, the remainder being unattacked. A careful examination of the chromic acid solution failed to reveal the presence of any derivative of phthalic acid. When treated with an acetic acid solution of hydrogen bromide (saturated at 0°) in a sealed tube at 100°, hydrolysis of the acetyl derivative took place, but no trace of a halogen derivative was formed, as would in all probability have been the case if a $\cdot CH_2 \cdot OAc$ group had been present (compare Perkin and Simonsen, T., 1904, **85**, 854; Müller, T., 1907, **91**, 1782).

Benzoylmorindone.—Morindone (1 gram) was mixed with pyridine (5 c.c.), and, after cooling in ice, benzoyl chloride (2 grams) was gradually added. The reaction proceeded readily, and, after remaining for thirty minutes, the mixture was poured into water, when a viscid oil separated, which rapidly solidified on triturating with hot alcohol. It was crystallised from acetic acid, when it was obtained in nodules of fine, yellow needles melting at 218—219°. For analysis, it was dried at 120°:

0·1079 gave 0·2924 CO_2 and 0·0403 H_2O. C = 73·9; H = 4·1.

$C_{36}H_{22}O_8$ requires C = 74·2; H = 3·8 per cent.

Methylation of Morindone: Morindone Monomethyl Ether and Trimethyl Ether.

Many experiments were made with a view to devise a satisfactory method for the preparation of morindone trimethyl ether. It was ultimately found that the following somewhat laborious process gave the best results.

Morindone (3 grams) was mixed with a solution of potassium

hydroxide (12 grams) dissolved in water (15 c.c.) and treated with methyl sulphate (15 c.c.), which was added all at once. The mixture was vigorously stirred, and when the reaction was complete, the same quantities of alkali and methyl sulphate were added. The alkaline solution, which was now deep red, was boiled, acidified, the crude methylation product collected, and again treated with alkali and methyl sulphate as before. The red solution contained in suspension a deep red, sparingly soluble potassium salt and the yellow trimethyl ether. It was filtered through cloth, and the residue boiled with dilute alkali and filtered, this treatment being repeated three times, when the filtrate should only be slightly red. The residue was ground with a considerable volume of chloroform, which dissolved the morindone trimethyl ether, leaving the insoluble, red potassium salt of the monomethyl ether *A* (see p. 773). The chloroform extract was evaporated, the crude, pale yellow trimethyl ether dissolved in hot toluene, and the toluene solution repeatedly washed with hot dilute alkali, which removed a further quantity of partly methylated morindone. (The alkaline washings were mixed with *A*.)

After separating from the alkali, the toluene solution was filtered, the toluene removed in a current of steam, when the nearly pure trimethyl ether was obtained. It was crystallised from acetic acid, when it separated in pale yellow needles melting at 229°, as stated by Oesterle and Tisza:

0·1013 gave 0·2566 CO_2 and 0·0426 H_2O. C = 69·1; H = 4·7.
$C_{18}H_{16}O_5$ requires C = 69·2; H = 5·1 per cent.

Morindone trimethyl ether, when pure, is insoluble in alkali; in sulphuric acid it dissolves to a deep blue solution.

The oxidation of morindone trimethyl ether has been carefully investigated. The ether was found to be extremely stable to chromic acid, and the greater part was recovered unchanged when oxidised with the equivalent quantity of oxidising agent, the remainder being apparently completely destroyed. When suspended in dilute sodium carbonate solution and boiled with a solution of potassium permanganate for several days, it was slowly oxidised. Much of the ether remained unattacked, and, with the exception of oxalic acid, no acid could be isolated in sufficient quantity for identification. When nitric acid was used as the oxidising agent, only oxalic acid appeared to be formed.

The sparingly soluble red potassium salt *A*, mentioned above, was suspended in hot water, decomposed with hydrochloric acid, and the brown solid which separated was collected. It was purified

by repeated crystallisation from acetic acid. For analysis, it was dried at 120°:

0·1012 gave 0·251 CO_2 and 0·0388 H_2O. C = 67·6; H = 4·2.
0·1028 ,, 0·2561 CO_2 ,, 0·038 H_2O. C = 67·9; H = 4·1.
$C_{16}H_{12}O_5$ requires C = 67·6; H = 4·2 per cent.

Morindone monomethyl ether crystallises in iridescent, brown needles melting at 248°. It is readily soluble in chloroform, toluene, or hot acetic acid, more sparingly so in ether or ethyl acetate, and very sparingly so in alcohol. It dissolves in concentrated sulphuric acid with a colour similar to that shown by morindone, only slightly redder. The sulphuric acid solution on the addition of a crystal of potassium nitrate gives a fine, greenish-red coloration. In fuming nitric acid, it dissolves with a transient red colour, yielding almost immediately a reddish-brown solution. It forms sparingly soluble red sodium and potassium salts, the solutions of which exhibited a slight fluorescence reminiscent of eosin. An attempt was made to determine the number of methoxy-groups present by the ordinary Zeisel method, but owing to the sparing solubility of the substance, the results were always low, although the heating was continued for from four to five hours and the hydriodic acid was mixed with acetic anhydride. Morindone monomethyl ether is readily attacked by an alkaline solution of potassium permanganate; it appears to undergo complete disintegration, and the bearing of this fact on the determination of the constitution of morindone has already been discussed.

Morindone monomethyl ether was also prepared by treating morindone with methyl iodide in the presence of sodium methoxide. Morindone (0·5 gram) was mixed with sodium methoxide (1·3 grams of sodium), and, after the addition of methyl iodide (0·8 gram), the mixture was heated in a sealed tube at 100° for eight hours. The deeply coloured product was poured into water, and, after the addition of potassium hydroxide solution, was boiled, filtered, and the residual potassium salt well washed with hot dilute alkali until the washings were only faintly coloured. The salt was decomposed with dilute hydrochloric acid, and the brown solid thus obtained (0·1 gram) was collected and recrystallised from acetic acid, when it melted at 247—248° and showed all the properties of morindone monomethyl ether. The melting point was not altered on admixture with an equal amount of the monomethyl ether prepared by means of methyl sulphate, as described above.

Diacetylmorindone Monomethyl Ether.—This substance was

readily prepared when the monomethyl ether was heated for two hours with acetic anhydride and anhydrous sodium acetate. It was crystallised from acetic acid and dried at 120° for analysis:

0·1042 gave 0·2494 CO_2 and 0·041 H_2O. C = 65·3; H = 4·3.

$C_{20}H_{15}O_7$ requires C = 65·2; H = 4·3 per cent.

Diacetylmorindone monomethyl ether separates from acetic acid in yellow, hexagonal prisms melting at 245—246°. It is sparingly soluble in hot alcohol.

The Sugars from Morindin.

In one experiment, the acid mother liquor from which the morindone had been separated was treated with sodium acetate until the excess of mineral acid was neutralised, and the solution concentrated to a small bulk. Excess of phenylhydrazine was added, and, after heating on the water-bath for one hour, the brownish-yellow osazone was collected. After repeated fractional crystallisation from alcohol, a sparingly soluble fraction was obtained which separated in fine yellow needles decomposing at 207°:

0·0689 gave 11 c.c. N_2 at 30° and 760 mm. N = 17·2.

$C_{17}H_{20}O_3N_4$ requires N = 17·1 per cent.

This substance would, therefore, appear to be the osazone of a pentose, and is possibly identical with the osazone (m. p. 202—203°) described by Perkin (*loc. cit.*, p. 150), but owing to the small quantity of material which was obtained in a pure state, great trust cannot be placed in the result of the analysis. From the mother liquor from which the above-mentioned osazone had been separated, a small quantity of another osazone was isolated, in stout yellow needles, which melted at about 195° and were readily soluble in alcohol.

The author wishes to thank Mr. M. Gopala Rau, M.A., for the care with which he made the analyses required for this and the following communication.

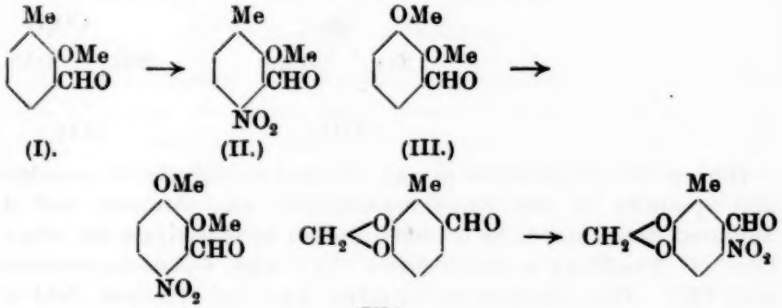
THE PRESIDENCY COLLEGE,
MADRAS.

[*Received, May 16th,* 1918.]

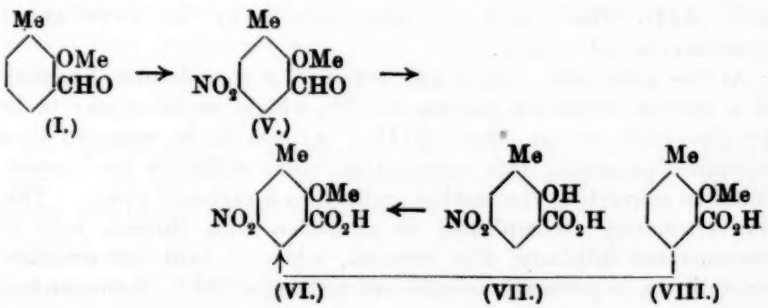
LXVII.—*The Nitration of* 2- *and* 6-*Methoxy*-m-*Tolualdehydes and* m-*Toluic Acids.*

By John Lionel Simonsen.

For synthetical experiments in the anthraquinone group, the author was desirous of preparing 3-methoxy-4-methylphthalic acid, and it appeared probable that the simplest method would be by nitrating 2-*methoxy*-m-*tolualdehyde* (I), when it was expected that the nitro-group would enter the ortho-position with respect to the aldehyde group with the formation of 4-nitro-2-methoxy-*m*-tolualdehyde (II), which could then be readily converted into the required acid, for it has been shown that *o*-veratraldehyde (III) and 5:6-methylenedioxy-*o*-tolualdehyde (IV), on nitration, yield nitro-derivatives containing the nitro-group in the ortho-position with respect to the aldehyde group (Perkin and Robinson, T., 1914, **105**, 2389; Perkin, T., 1916, **109**, 910).

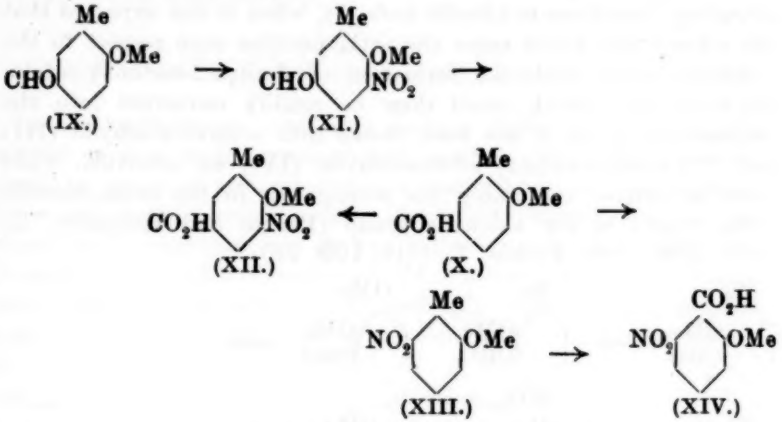


This expectation was not, however, realised, for when 2-methoxy-*m*-tolualdehyde was treated with nitric acid under the conditions described in the experimental part of this paper (see p. 778), an almost quantitative yield of 5-*nitro*-2-*methoxy*-m-*tolualdehyde* (V) was obtained.



The constitution of this aldehyde was readily proved by the fact that on oxidation it was converted into 5-*nitro*-2-*methoxy*-m-*toluic acid* (VI), an acid which was readily obtained by the methylation of 5-nitro-2-hydroxy-*m*-toluic acid (VII) (Einhorn and Pfyl, *Annalen*, 1900, **311**, 47; Fortner, *Monatsh.*, 1901, **22**, 939).

5-Nitro-2-methoxy-*m*-toluic acid was also prepared by the nitration of 2-*methoxy*-m-*toluic acid* (VIII), which was obtained by the oxidation of the aldehyde.



During the preparation of the 2-hydroxy-aldehyde, a considerable quantity of the 6-hydroxy-aldehyde was obtained, and it appeared, therefore, to be of some interest to investigate the nitration of 6-methoxy-*m*-tolualdehyde (IX) and 6-methoxy-*m*-toluic acid (X). The aldehyde on nitration gave an excellent yield of the 5-*nitro*-derivative (XI), the constitution of which was proved by the fact that on treatment with acetone and alkali it yielded the corresponding derivative of distyryl ketone, no formation of indigotin taking place, which would have been the case if the nitro-group had entered either of the positions ortho to the aldehyde group. The nitro-aldehyde yielded on oxidation the corresponding *acid* (XII), which acid was also formed by the nitration of 6-methoxy-*m*-toluic acid.

At the same time, there was obtained a considerable quantity of a neutral substance melting at 69°, which would appear to be 6-*nitro*-o-*tolyl methyl ether* (XIII). As was to be expected of a substance possessing this constitution, some difficulty was experienced in converting the methyl group into a carboxyl group. This was ultimately accomplished by oxidation with chromic acid in concentrated sulphuric acid solution, when an acid was obtained crystallising in prismatic needles and melting at 161°. Simonsen and

Rau (T., 1916, **111**, 223 *et seq.*) have described three of the four possible isomeric nitro-2-methoxybenzoic acids; this acid was found not to be identical with any of the three, and it is in all probability *6-nitro-2-methoxybenzoic acid* (XIV). Unfortunately, it was not obtained in sufficient quantity for a detailed examination to be made.

The results described above are of some interest in illustrating the difference in orientating effect of methyl and methoxy-groups. It has been suggested (Simonsen and Rau, *loc. cit.*) that a negative group in the ortho-position with respect to a positive group tends to neutralise such a grouping, and the orientating effect is then in the main exercised by the remaining positive group in the molecule. Whilst this appears to be the case in the nitration of acetylamino-methoxy-derivatives and also of other methoxy-derivatives, the rule is evidently not of any general application.

EXPERIMENTAL.

2-*Methoxy*-m-*tolualdehyde* (I).

The phenolic aldehyde (10 grams) was dissolved in sodium methoxide (2 grams of sodium) and treated with methyl sulphate (15 grams), the addition of the same quantities of alkali and methyl sulphate being repeated three times. The solution was then heated on the water-bath for fifteen minutes to complete the decomposition of the methyl sulphate, water added, the methoxy-aldehyde extracted with ether, and the ethereal solution dried and evaporated.

2-*Methoxy*-m-*tolualdehyde* was obtained as a viscid, pleasant-smelling oil which boiled at about 120°/6 mm. With concentrated sulphuric acid it gave a cherry-red coloration.

The *oxime* was best prepared by dissolving the aldehyde (1·3 grams) in alcohol, and, after the addition of hydroxylamine hydrochloride (2 grams) and sodium acetate (2 grams), the mixture was heated on the water-bath for half an hour. On pouring into water, the oxime separated in silky needles, which were purified by crystallisation from methyl alcohol. It melted at 118°:

0·1558 gave 12·9 c.c. N_2 at 33° and 759 mm. N = 8·7.
$C_9H_{11}O_2N$ requires N = 8·5 per cent.

The *semicarbazone*, prepared in the usual manner, crystallised from alcohol, in which it was somewhat sparingly soluble, in white, microscopic needles melting at 224°:

0·0906 gave 16·8 c.c. N_2 at 30° and 760 mm. N = 20·0.
$C_{10}H_{13}O_2N_3$ requires N = 20·2 per cent.

Nitration of 2-*Methoxy*-m-*tolualdehyde*. 5-*Nitro*-2-*methoxy*-m-*tolualdehyde* (V).

In one experiment, the aldehyde (2 grams) was added gradually to nitric acid (D 1·52: 10 grams), which was kept well cooled in ice. The reaction proceeded smoothly, and, after remaining for fifteen minutes, the mixture was poured on ice, when an oil separated which rapidly solidified. This was collected, triturated with dilute sodium carbonate solution* to remove a trace of acid, dried on porous porcelain, and purified by crystallisation from a mixture of ether and light petroleum (yield, 2·2 grams):

0·1634 gave 10·7 c.c. N_2 at 30° and 759 mm. N = 7·0.
$C_9H_9O_4N$ requires N = 7·2 per cent.

5-*Nitro*-2-*methoxy*-m-*tolualdehyde* crystallises in balls of needles melting at 61—62°. It is readily soluble in the ordinary organic solvents with the exception of light petroleum, in which it is somewhat sparingly soluble. The 5-nitro-aldehyde was found to be the sole product of the reaction, since no trace of an isomeride could be isolated from the mother liquors.

The *semicarbazone* crystallised from alcohol in fine, woolly needles which decomposed at 233°:

0·0948 gave 19·4 c.c. N_2 at 32° and 758 mm. N = 22·0.
$C_{10}H_{12}O_4N_4$ requires N = 22·2 per cent.

5 : 5′-*Dinitro*-2 : 2′-*dimethoxydi*-3-m-*methylstyryl Ketone*,
$NO_2 \cdot C_6H_2Me(OMe) \cdot CH{:}CH \cdot CO \cdot CH{:}CH \cdot C_6H_2Me(OMe) \cdot NO_2$.

This substance was readily prepared under the following conditions: the aldehyde (0·5 gram), dissolved in warm methyl alcohol (5 c.c.), was mixed with acetone (0·5 gram), and, after the addition of potassium hydroxide (50 per cent.: two drops), the yellow mixture was heated to boiling for a few minutes. The liquid rapidly clouded and a voluminous mass of yellow needles separated. These were collected, well washed with methyl alcohol, and the residue recrystallised from acetic acid, in which it was only very sparingly soluble, when it was obtained in fine, yellow needles decomposing at 252°:

0·094 gave 6 c.c. N_2 at 32° and 758 mm. N = 6·8.
$C_{21}H_{20}O_7N_2$ requires N = 6·8 per cent.

* The acid (0·05 gram) which separated from the sodium carbonate solution on acidification was found to be 5-nitro-2-methoxy-*m*-toluic acid.

Oxidation of 5-*Nitro*-2-*methoxy*-m-*tolualdehyde*. 5-*Nitro*-2-*methoxy*-m-*toluic Acid* (VI).

The nitro-aldehyde (1·2 grams) was dissolved in acetone (30 c.c.) and finely powdered potassium permanganate (0·65 gram) was gradually added. The oxidation proceeded readily, and, after the reaction was complete, water was added, the solution boiled, and the manganese dioxide filtered off. The filtrate was concentrated on the water-bath until free from acetone, a trace of unchanged aldehyde removed, and the aqueous solution acidified, when the nitro-acid separated in fine needles. These were collected and crystallised from hot water:

0·2036 gave 12 c.c. N_2 at 30° and 759 mm. N = 6·3.
$C_9H_9O_5N$ requires N = 6·6 per cent.

5-*Nitro*-2-*methoxy*-m-*toluic acid* crystallises from hot water in glistening, silky needles melting at 154°. It is readily soluble in the ordinary organic solvents with the exception of light petroleum.

The *silver* salt separated in pale yellow needles, which were somewhat soluble in hot water:

0·2974 gave 0·1007 Ag. Ag = 33·8.
$C_9H_8O_5NAg$ requires Ag = 34·0 per cent.

For the purposes of comparison, a specimen of 5-nitro-2-methoxy-*m*-toluic acid was prepared by the methylation of the corresponding hydroxy-acid obtained by the nitration of 2-hydroxy-*m*-toluic acid (Einhorn and Pfyl, *loc. cit.*). The acid isolated from the methylation melted at 154°, and was identical in every way with the acid prepared by the method described above.

2-*Methoxy*-m-*toluic Acid* (VIII).

This acid was readily obtained by the oxidation of the corresponding aldehyde by means of potassium permanganate in acetone solution. It separated from hot water in hair-like needles which melted at 83°. It was readily soluble in hot water and in the ordinary organic solvents, somewhat readily so in cold water:

0·0952 gave 0·2266 CO_2 and 0·053 H_2O. C = 64·9; H = 6·2.
$C_9H_{10}O_3$ requires C = 65·1; H = 6·1 per cent.

The *silver* salt was obtained as a caseous, white precipitate which was dried at 100° for analysis:

0·37 gave 0·1475 Ag. Ag = 39·9.
$C_9H_9O_3Ag$ requires Ag = 39·6 per cent.

Nitration of 2-Methoxy-m-toluic Acid.

The acid (0·3 gram) was gradually added to nitric acid (D 1·52: 1 gram), the temperature being kept at about 30°. After remaining for ten minutes, the clear solution was poured into water, when the nitro-acid separated and was collected (yield, 0·3 gram). After crystallisation from hot water, it melted at 154°, and this melting point was unaltered on admixture with a specimen of the 5-nitro-acid prepared by the oxidation of the nitro-aldehyde as described above. The 5-nitro-acid appeared to be the sole product of the reaction, since the mother liquors yielded no trace of an isomeride.

Nitration of 6-Methoxy-m-tolualdehyde (IX). *5-Nitro-6-methoxy-m-tolualdehyde* (XI).

The aldehyde (3 grams) was added slowly to nitric acid (D 1·52: 9 grams), which was kept well cooled in a mixture of salt and ice. The aldehyde dissolved with considerable evolution of gas, and, after remaining for ten minutes, the mixture was poured on ice, when the nitro-aldehyde separated and was collected (yield, 4·2 grams).

5-Nitro-6-methoxy-m-tolualdehyde crystallises from dilute alcohol in small needles melting at 77°. It is readily soluble in all the ordinary organic solvents:

0·1093 gave 7·2 c.c. N_2 at 31° and 760 mm. N = 7·1.

$C_9H_9O_4N$ requires N = 7·2 per cent.

The *semicarbazone* crystallised from alcohol in needles which decomposed at 235°:

0·0849 gave 17·4 c.c. N_2 at 31° and 760 mm. N = 22·0.

$C_{10}H_{12}O_4N_4$ requires N = 22·2 per cent.

5:5′-Dinitro-4:4′-dimethoxydi-3-methylstyryl Ketone.

This substance was prepared in a similar manner to the isomeride described on p. 778. It crystallises from acetic acid in yellow needles melting at 214°:

0·0526 gave 3·4 c.c. N_2 at 30° and 759 mm. N = 6·9.

$C_{21}H_{20}O_7N_2$ requires N = 6·8 per cent.

5-Nitro-6-methoxy-m-toluic Acid (XII).

This acid was readily obtained when the nitro-aldehyde was oxidised with potassium permanganate in acetone solution. For analysis, it was crystallised from dilute alcohol:

0·1752 gave 11·2 c.c. N_2 at 31° and 760 mm. N = 6·8.
$C_9H_9O_5N$ requires N = 6·6 per cent.

5-Nitro-6-methoxy-m-*toluic acid* crystallises in colourless, felted needles melting at 180—181°, and softening slightly at 175°. It is very sparingly soluble in cold water, somewhat more readily so in hot; it is very readily soluble in chloroform, acetic acid, or ethyl acetate, more sparingly so in benzene.

The *barium* salt crystallised in sparingly soluble, curious nodular masses of needles; the *calcium* salt was obtained in stellate clusters of needles which were readily soluble in hot water; the *silver* salt separated as a granular, white precipitate:

0·2272 gave 0·0772 Ag. Ag = 34·0.
$C_9H_8O_5NAg$ requires Ag = 34·0 per cent.

The *methyl* ester, $C_{10}H_{11}O_5N$, crystallised from dilute methyl alcohol in silky needles melting at 47°.

Nitration of 6-Methoxy-m-*toluic Acid* (X).

The finely powdered acid (1·4 grams) was gradually added tc nitric acid (D 1·52 : 5 grams), the temperature being kept between 30° and 35°. The acid dissolved with considerable evolution of gas, and, after remaining for ten minutes, the mixture was poured into water and the solid which separated was collected and triturated with dilute sodium carbonate solution, a considerable quantity of a neutral substance, *A* (0·62 gram), remaining undissolved. This was separated, the filtrate acidified, and the acid which was deposited (0·97 gram) crystallised from dilute alcohol, when it was obtained in fine needles melting at 180—181°, this melting point being unaltered on admixture with a specimen of the acid obtained by the oxidation of the nitro-aldehyde. The neutral substance *A* was purified by crystallisation from methyl alcohol, from which it separated in glistening needles melting at 69°. For analysis, it was dried in a vacuum:

0·1404 gave 11 c.c. N_2 at 30° and 759 mm. N = 8·5.
$C_8H_9O_3N$ requires N = 8·4 per cent.

This substance would appear to be *6-nitro-o-tolyl methyl ether* (XIII). It was attacked by a hot alkaline solution of potassium permanganate only with great difficulty, but it was found to be readily oxidised by chromic acid under the following conditions: the nitro-compound (0·25 gram) was dissolved in concentrated sulphuric acid (1 c.c.) and gradually treated with chromic acid (0·3 gram) dissolved in concentrated sulphuric acid (2 c.c.), the temperature being kept at about 40°. When the reaction was

complete, water was added, the nitro-acid which separated was collected, dissolved in a little dilute sodium carbonate solution, and filtered from a little unattacked material. On acidifying the alkaline filtrate, the *nitro-acid* separated in fine, prismatic needles which melted at 159—160°. After crystallisation from hot water, in which it was readily soluble, it melted at 161°. This acid was probably 6-*nitro*-2-*methoxybenzoic acid* (XIV), an acid which does not appear to have been described previously. It was not identical with 5-nitro-2-methoxybenzoic acid, which also melts at this temperature (Simonsen and Rau, T., 1917, **111**, 228), since a mixture of the two acids melted at about 140°. Unfortunately, this new acid was not obtained in sufficient quantity for a detailed examination.

In conclusion, the author wishes to thank Mr. M. Gopala Rau, M.A., for his assistance in the analytical work.

THE PRESIDENCY COLLEGE,
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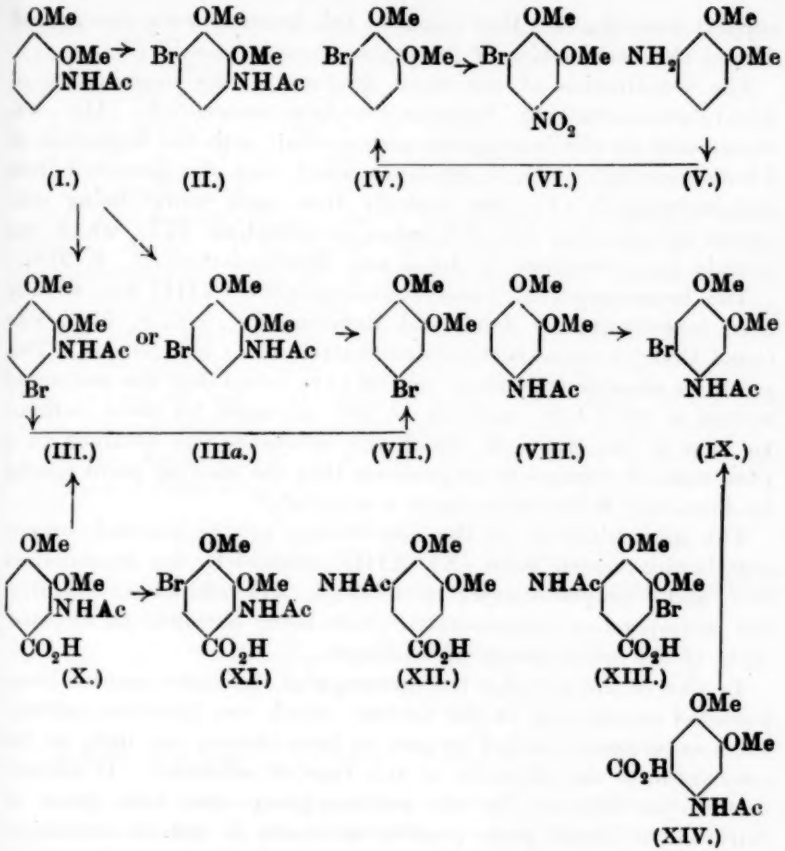
LXVIII.—*The Bromination of some Derivatives of Veratrole.*

By JOHN LIONEL SIMONSEN and MADYAR GOPALA RAU.

IN previous communications (T., 1917, **111**, 69, 220; this vol., p. 22), the results of experiments were described on the nitration of some acetylamino-derivatives of veratrole and methoxybenzoic acids, and attention was directed to the relative orientating influence of methoxy-groups having positive or negative groups in the ortho- or para-positions. In continuation of these experiments, it appeared to us to be a matter of some interest to investigate the effect of bromination on the same series of compounds in order to determine whether substitution would proceed similarly. When these experiments were nearing completion, a paper by Jones and Robinson (T., 1917, **111**, 903) appeared which has anticipated our work in some directions.

We selected for our experiments the two isomeric acetylaminoveratroles and the three acetylaminoveratric acids, and the results obtained are shown diagrammatically below.



The bromination was performed either in chloroform or in glacial acetic acid solution, the sparingly soluble bromo-amide which separated was decomposed with water, and the product isolated in a suitable manner. As will be observed, the bromine always entered the nucleus in the para-position with respect to the acetylamino-group, except in the case of 6-acetylaminoveratric acid (XIV), when, this position being already occupied, the carboxyl group was eliminated with the formation of 5-bromo-4-acetylaminoveratrole (IX). Only in one case was the formation of an isomeride detected, namely, when 3-acetylaminoveratrole (I) was brominated under special conditions (see p. 786). It has not, unfortunately, proved possible to orientate this isomeride, which must be either the 4- or 5-bromo-derivative (III or III*a*), since on the elimination of the amino-group it yielded 4-bromoveratrole. From analogy, it is most probably the 4-isomeride, and this view receives

support from the fact that traces of this bromide were also formed during the bromination of 2-acetylaminoveratric acid (X).

The constitution of the main product of the bromination of 3-acetylaminoveratrole, 6-*bromo*-3-*acetylaminoveratrole* (II), was determined by eliminating the amino-group with the formation of 3-*bromoveratrole* (IV), a substance which was also prepared from 3-aminoveratrole (V), the bromide from each source being converted by nitration into 6-bromo-4-nitroveratrole (VI), which has already been described by Jones and Robinson (*loc. cit.*, p. 918).

The bromination of 4-acetylaminoveratrole (VIII) has already been investigated by Jones and Robinson (*loc. cit.*, p. 913), who found that 5-bromo-4-acetylaminoveratrole (IX) was formed. This result we are able to confirm, but we have found that the compound melted at 127—128°, and not at 140° as stated by these authors. In view of the ease with which this substance was obtained in a pure state, it appears to us probable that the melting point quoted by Jones and Robinson is due to a misprint.*

The determination of the constitution of the isomeric bromo-acetylaminoveratric acids (XI, XIII) obtained by the bromination of 2- and 5-acetylaminoveratric acids (X, XII) offered no difficulty, the corresponding bromoveratric acids being obtained on displacement of the amino-group by hydrogen.

In view of the fact that the formation of the bromo-amide always preceded substitution in the nucleus, which was therefore indirect, these experiments cannot be said to have thrown any light on the mechanism of the nitration of this type of substance. If indirect substitution directed by the methoxy-group does take place on nitration, it should prove possible by choice of suitable conditions to isolate this salt, and it is hoped to make further experiments with the object of throwing light on this problem.

Experimental.

Bromination of 3-*Acetylaminoveratrole* (I). 6-*Bromo*-3-*acetylaminoveratrole* (II).

In one experiment, 3-acetylaminoveratrole (3 grams) was dissolved in chloroform (9 c.c.), and to the ice-cold solution bromine (2·64 grams) dissolved in chloroform (3 c.c.) was gradually added, when bromination took place readily with the separation of the sparingly soluble yellow bromo-amide. After remaining for fifteen minutes, the precipitate was decomposed by the addition of water, the chloroform solution separated, washed with a little

* Prof. Robinson has since informed me that this is the case.—J. L. S.

dilute alkali, dried, and evaporated, when a theoretical yield of the bromoacetylamine was obtained. It was purified by crystallisation from dilute acetic acid:

0·1942 gave 0·1332 AgBr. Br = 29·3.

0·1544 „ 7·6 c.c. N_2 at 30° and 758 mm. N = 5·3.

$C_{10}H_{12}O_3NBr$ requires Br = 29·2; N = 5·1 per cent.

6-*Bromo*-3-*acetylaminoveratrole* crystallises in prismatic needles melting at 78°. It is readily soluble in all the ordinary organic solvents with the exception of benzene and light petroleum. The same bromoacetylamine was found to be the sole product when glacial acetic acid was used as the solvent in place of chloroform.

6-*Bromo*-3-*aminoveratrole* was formed when the acetyl derivative was heated on the water-bath for some hours with hydrochloric acid (50 per cent.). It crystallises from dilute methyl alcohol in colourless needles melting at 66°, and is readily soluble in the ordinary organic solvents:

0·119 gave 6·6 c.c. N_2 at 30° and 759 mm. N = 6·0.

$C_8H_{10}O_2NBr$ requires N = 6·0 per cent.

The *benzoyl* derivative crystallised from dilute alcohol in minute, radiating needles melting at 75°:

0·1935 gave 8·0 c.c. N_2 at 30° and 760 mm. N = 4·4.

$C_{15}H_{14}O_3NBr$ requires N = 4·1 per cent.

3-*Bromoveratrole* (IV) *and* 6-*Bromo*-4-*nitroveratrole* (VI).

1. For the determination of the constitution of the bromo-amide described above, it was necessary to prepare 3-*bromoveratrole*. This substance, which does not appear to have been previously described, was readily obtained when 3-aminoveratrole (Gibson, Simonsen, and Rau, *loc. cit.*, p. 79) was diazotised and treated with cuprous bromide in the usual manner. It was purified by distillation in a current of steam and subsequent distillation under diminished pressure, when it was obtained as a somewhat viscid oil boiling at 114°/5 mm.:

0·1287 gave 0·1117 AgBr. Br = 36·9.

$C_8H_9O_2Br$ requires Br = 36·9 per cent.

When 3-bromoveratrole was dissolved in acetic acid and treated with nitric acid (D 1·4), it yielded 6-bromo-4-nitroveratrole, which crystallised from alcohol in needles melting at 112—113°, and was found by direct comparison to be identical with the substance described by Jones and Robinson (*loc. cit.*, p 918) (Found: N = 5·5. Calc.: N = 5·3 per cent.).

II. 3-Bromoveratrole was also formed when 6-bromo-3-amino-

veratrole (see above) was diazotised in alcoholic solution with amyl nitrite in the usual manner. It was identified by conversion into 6-bromo-4-nitroveratrole melting at 112—113° (Found: N = 5·5. Calc.: N = 5·3 per cent.).

4- or 5-*Bromo*-3-*acetylaminoveratrole* (III or III*a*).

For the preparation of this substance, the following method was found to be the most convenient. The acetylamine (5 grams) was dissolved in acetic acid (50 per cent.: 20 c.c.) and bromine (4·2 grams) was gradually added to the well-cooled solution. When bromination was complete, the mixture was diluted with water and ammonia added until a nearly neutral solution was obtained. On remaining overnight, the bromination product, *A*, separated; this was collected and the filtrate repeatedly extracted with ether. The ether was evaporated and the residual oil triturated with cold acetone, when a sparingly soluble solid remained. This was mixed with the product *A* (see above) and purified by crystallisation from acetone, when it separated in well-defined octahedra melting at 151° (yield, 2 grams):

0·1966 gave 0·136 AgBr. Br = 29·4.
0·1842 ,, 9·4 c.c. N_2 at 30° and 756 mm. N = 5·3.
$C_{10}H_{12}O_3NBr$ requires Br = 29·2; N = 5·1 per cent.

4- or 5-Bromo-3-acetylaminoveratrole is readily soluble in alcohol or acetic acid, more sparingly so in benzene, acetone, ether, or light petroleum.

The corresponding *amine* was obtained by heating the acetyl derivative for one hour on the water-bath with sulphuric acid (50 per cent.). It separated from dilute methyl alcohol in colourless needles melting at 49°:

0·1268 gave 0·1023 AgBr. Br = 34·4.
$C_8H_{10}O_2NBr$ requires Br = 34·4 per cent.

The *benzoyl* derivative, $C_{15}H_{14}O_3NBr$, crystallised from dilute alcohol in needles melting at 146°.

The *platinochloride* separated from dilute hydrochloric acid in aggregates of yellowish-brown prisms which darkened at 200° and gradually decomposed when heated above this temperature:

0·1659 gave 0·0402 Pt. Pt = 24·2.
$(C_8H_{10}O_2NBr)_2H_2PtCl_4$ requires Pt = 24·3 per cent.

When the above-mentioned bromo-amine was diazotised, it yielded 4-bromoveratrole, which was identified by conversion into 4-bromo-5-nitroveratrole melting at 123° (Jones and Robinson,

loc. cit., give 125° as the melting point of this substance (Found: N=5·3. Calc.: N=5·2 per cent.).

The acetone solution from which the 4- or 5-bromo-3-acetylaminoveratrole had been separated was evaporated, and the residue (5·5 grams) was repeatedly crystallised from alcohol, when a substance melting at 78° was isolated and found by direct comparison to be 6-bromo-3-acetylaminoveratrole.

Bromination of 4-Acetylaminoveratrole (VIII). *5-Bromo-4-acetylaminoveratrole* (IX).

As has already been mentioned in the introduction (p. 784), the bromination of 4-acetylaminoveratrole has already been investigated by Jones and Robinson (*loc. cit.*, p. 913), who found that 5-bromo-4-acetylaminoveratrole was formed. We have investigated this bromination both in chloroform and in acetic acid solutions, when the 5-bromo-derivative was obtained as the sole product. It crystallised from hot water in long, slender needles which melted at 127—128°. Attention has already been directed to the discrepancy between this melting point and that found by Jones and Robinson:

0·1981 gave 0·1352 AgBr. Br=29·3.

$C_{10}H_{12}O_3NBr$ requires Br=29·2 per cent.

5-Bromo-4-aminoveratrole, which has not been described previously, was obtained only with considerable difficulty, owing to the ease with which it decomposed. Ultimately, the following method was found to be fairly satisfactory. The bromoacetylamine was dissolved in a methyl-alcoholic solution of potassium hydroxide (15 per cent. KOH) and heated on the water-bath for three hours, the excess of potassium hydroxide removed by carbon dioxide, the solution filtered, and the methyl alcohol evaporated in a vacuum at the ordinary temperature. The residue was extracted with ether, the ether evaporated, when the base was obtained as a viscid oil which rapidly crystallised. After draining on porous porcelain, it was recrystallised from dilute methyl alcohol, from which it separated in colourless needles melting at 51°. When exposed to the air, the base rapidly darkened in colour:

0·0844 gave 0·0682 AgBr. Br=34·4.

$C_8H_{10}O_2NBr$ requires Br=34·4 per cent.

The *benzoyl* derivative, $C_{15}H_{14}O_3NBr$, crystallised in needles melting at 142°.

The constitution of this bromo-amine was readily determined by conversion into 4:5-dibromoveratrole. The bromo-amine (1 gram) was dissolved in hydrobromic acid (30 per cent.: 5 c.c.) and diazo-

tised by the addition of sodium nitrite (0·4 gram). After remaining in the cold for half an hour, the mixture was poured into hydrobromic acid (5 c.c.) containing a little copper powder and allowed to remain in the cold overnight. The solution was warmed on the water-bath, extracted with ether, the ether evaporated, and the residue crystallised from alcohol, when 4:5-dibromoveratrole separated in needles melting at 92°, which melting point was not changed on admixture with a specimen of the compound obtained from a different source.

Bromination of 2-*Acetylaminoveratric Acid* (X). 5-*Bromo*-2-*acetylaminoveratric Acid* (XI).

I. 2-Acetylaminoveratric acid (2 grams) was suspended in acetic acid (4 c.c.) and mixed with bromine (1·3 grams) dissolved in acetic acid (2 c.c.); the mixture was sealed up and allowed to remain, with occasional shaking, for twenty-four hours, when the colour of the bromine had completely disappeared and a yellow, unstable bromo-amide had separated. On the addition of water, a clear solution was obtained, from which the bromo-acid gradually crystallised. This was collected, and a further quantity obtained by extracting the filtrate with ether (yield, 2·1 grams). On trituration with dilute sodium carbonate solution, a small quantity of a neutral substance (0·1 gram) remained undissolved. This crystallised from alcohol in needles melting at about 168°, but it was not obtained in sufficient quantity for investigation. The acid which separated from the alkaline filtrate on acidification was found to be quite homogeneous, and was purified by crystallisation from ethyl acetate:

0·1534 gave 0·0908 AgBr. Br = 25·2.

$C_{11}H_{12}O_5NBr$ requires Br = 25·1 per cent.

5-*Bromo*-2-*acetylaminoveratric acid* separates in fine needles melting at 188—189°. It is readily soluble in acetone, alcohol, ethyl acetate, or chloroform, more sparingly so in water, benzene, or ether, and very sparingly so in light petroleum

II. 2-Acetylaminoveratric acid (2 grams) was mixed with chloroform (4 c.c.) and treated with bromine (1·3 grams) dissolved in chloroform (2 c.c.); the bromo-amide gradually separated, and, after remaining for twenty-four hours, the mixture was treated with water, the chloroform separated, washed with a little dilute alkali, dried, and evaporated, when a small quantity of a neutral substance remained. This was crystallised from a little dilute methyl alcohol, when it crystallised in octahedra melting at 151°, and was found to be 4- or 5-bromo-3-acetylaminoveratrole.

The alkaline washings yielded on acidification 5-bromo-2-acetylaminoveratric acid.

5-Bromo-2-aminoveratric acid was obtained when the acetyl derivative was hydrolysed with either hydrochloric acid or concentrated sulphuric acid. It crystallises from alcohol in colourless prisms melting at 158—159°:

0·1114 gave 5·6 c.c. N_2 at 31° and 758 mm. N = 5·4.
$C_9H_{10}O_4NBr$ requires N = 5·1 per cent.

The constitution of this amino-acid was readily proved by the elimination of the amino-group, when 5-bromoveratric acid melting at 191° was obtained (Found: Br = 30·5. Calc.: Br = 30·6 per cent.).

Bromination of 5-Acetylaminoveratric Acid (XII).
2-Bromo-5-acetylaminoveratric Acid (XIII).

The acid (2 grams) was dissolved in acetic acid (4 c.c.) and treated with the calculated quantity of bromine dissolved in a little acetic acid. The clear solution rapidly became cloudy, and a voluminous precipitate of the reddish-yellow bromo-amide separated. After remaining for ten minutes, water was carefully added, when a clear solution was obtained, from which the bromo-acd slowly crystallised. This was collected and recrystallised from dilute alcohol, from which it separated in fine needles:

0·1862 gave 0·1096 AgBr. Br = 25·1.
$C_{11}H_{12}O_5NBr$ requires Br = 25·1 per cent.

2-Bromo-5-acetylaminoveratric acid melts at 221°. It is readily soluble in hot alcohol or acetone, more sparingly so in the cold solvents; in water or benzene it is sparingly soluble.

On hydrolysis of the acetylamino-acid with hydrochloric acid (50 per cent.), the *amino*-acid was obtained as a viscid oil which rapidly crystallised. It was recrystallised from dilute alcohol, from which it separated in glistening prisms melting at 183°. It is readily soluble in hot alcohol or acetone, but only sparingly so in water, chloroform, or benzene:

0·151 gave 0·1021 AgBr. Br = 28·8.
$C_9H_{10}O_4NBr$ requires Br = 28·9 per cent.

When diazotised in alcoholic solution with amyl nitrite, it yielded 2-bromoveratric acid, which after crystallisation from methyl alcohol melted at 201—202° (Found: Br = 30·2. Calc.: Br = 30·6 per cent.).

Bromination of 6-*Acetylaminoveratric Acid* (XIV). 5-*Bromo*-4-*acetylaminoveratrole* (IX).

The finely divided acid (2 grams) was suspended in chloroform and the calculated quantity of bromine dissolved in chloroform gradually added. The bromine was rapidly absorbed, and simultaneously a small amount of gas (carbon dioxide) was evolved. After remaining overnight, water was added to the pasty mass, when a vigorous evolution of gas was observed. A small quantity of unchanged acid was removed by filtration, the chloroform separated, washed with a little dilute alkali, dried, and evaporated. The deep brown residue rapidly solidified to a hard, crystalline cake, and was purified by crystallisation from hot water, from which it separated in slender, colourless needles melting at 127—128°, and was identical in every way with the compound obtained by the bromination of 4-acetylaminoveratrole. No trace of any other product could be isolated:

0·1144 gave 0·0775 AgBr. Br = 28·9.

$C_{10}H_{12}O_3NBr$ requires Br = 29·2 per cent.

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LXIX.—*The Electrical Conductivity of Acids and Bases in Aqueous Solutions.*

By JNANENDRA CHANDRA GHOSH.

IN previous papers (this vol., pp. 449, 627, 707), it has been shown that the variation of equivalent conductivity with dilution, in the case of all binary univalent salts, is represented by the equation

$$\frac{N.E^2\sqrt[3]{2N}}{D.\sqrt[3]{V}} = 2RT \log_e \frac{\mu_\infty}{\mu_v} \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where N is Avogadro's number, E the absolute charge on an ion, D the dielectric constant of the solvent, and V the dilution.

Abnormally High Values of Activity-coefficients of Acids and Bases.—Aqueous solutions of strong acids like hydrochloric or nitric acids, and of strong bases like sodium or potassium hydroxides, however, prove exceptions to the above rule. This irregular behaviour will be at once evident from table I, where the values of the activity-coefficients calculated from equation (1) are com-

pared with the observed values (Noyes and Falk, *J. Amer. Chem. Soc.*, 1912, **34**, 474).

TABLE I.

	$V=$	10.	20.	50.	100.	200.	500.
$\frac{\mu_v}{\mu_\infty}$	calc.	0·844	0·875	0·906	0·924	0·940	0·955
$\frac{\mu_v}{\mu_\infty}$	obs. for HCl.....	0·925	0·944	0·962	0·972	0·981	0·988
$\frac{\mu_v}{\mu_\infty}$	obs. for KOH ...	0·887	0·910	0·933	0·945	—	0·970

This irregularity disappears as we pass from the aqueous to non-aqueous solutions of strong acids. In alcoholic solutions, for example, equation (1) is exactly followed. In table II, the observed values of the molecular conductivity of hydrochloric acid in methyl alcohol are taken from the work of Goldschmidt and Thuesen (*Zeitsch. physikal. Chem.*, 1912, **81**, 32). For dilute solutions, the agreement between observed and calculated values is always within 1 per cent., and the validity of equation (1) is therefore proved beyond doubt.

TABLE II. $T=25°$.

	$V=$	40.	80.	160.	320.	640.
μ_∞ calc. from $\mu_{80}=192·2$	μ_v calc.	142·5	151·8	159·5	166·7	170·9
μ_∞ obtained by extrapolation $=192·1$	μ_v obs.	141·0	151·8	160·5	167·2	171·9

Abnormally High Values of the Electrical Conductivity of Acids and Bases.—It has always appeared remarkable that the values of the equivalent conductivity of acids and bases in aqueous solutions are not of the same order of magnitude as those of other salts. Thus the conductivities of hydrogen and hydroxyl ions in aqueous solutions are 318 and 175 respectively at 18°, whilst those of the other ions never exceed 70. In non-aqueous solutions, again, this abnormality is not observed. Thus in ethyl alcohol, the conductivities of hydrogen and hydroxyl ions are 32·1 and 16·5, whilst those of potassium and ammonium ions are 21·5 and 20 respectively (Godlewski, *Zeitsch. physikal. Chem.*, 1905, **51**, 751; Hägglund, *Arkiv. Kem. Min. Geol.*, 1911, **4**, No. 11). Here the values are of the same order. This is also true for solutions in other solvents, for example, methyl alcohol or acetone.

The Conductivity of Aqueous Solutions of Acids and Bases—not entirely a Convection Process.—It is thus evident that the abnormal conductivities of hydrogen and hydroxyl ions, in aqueous solutions,

are somehow related to the high values of the activity-coefficients of acids and bases, both these abnormalities disappearing when the solvent medium is other than water. Equation (1) has a good theoretical basis, and it appears more reasonable to assume that the observed ratio $\frac{\mu_v}{\mu_\infty}$ for acids and bases in aqueous solutions is not a real expression for the activity-coefficient, than to impugn its validity. It appears to the author that the observed conductivity of hydrogen and hydroxyl ions in water is the additive effect of two separate and independent processes, namely, (1) the transference of electricity by the convection of charged bodies, and (2) the transference of electric charge through molecules of water by the alternate processes of dissociation and recombination during impact with hydrogen or hydroxyl ion.

The first process is, of course, the ordinary method of electrolytic conduction met with in salt solutions. Here, only the free ions take part in the transference of electricity, and their number is given by the equation

$$N' = 2N \cdot e^{-\frac{A}{2RT}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

The mechanism of transport of electricity through molecules of water may be conceived as follows.

A molecule of water is capable of dissociating into hydrogen and hydroxyl ions, the only ions that possess abnormal conductivity. Now, in a dilute solution of hydrochloric acid the hydrogen ion is surrounded by water molecules on all sides. It appears probable that when a hydrogen ion strikes against a molecule of water, the latter in some cases undergoes dissociation. The hydrogen ion thus produced carries away the electric charge by convection, whilst the hydroxyl ion of the water molecule combines with the impinging hydrogen ion to generate a molecule of water. The conception of the process is similar to that imagined by Grotthuss to explain the phenomenon of electrolytic conduction. It may well be that the hydrogen atom of the water molecule, which is farthest from the point of impact, shoots off as a charged particle, and if the process of dissociation and recombination is instantaneous, the electric charge $(+E)$ appears to be carried instantaneously through a distance proportional to the diameter S of the water molecule. Thus at each impact attended with dissociation a distance K_1S is saved, where K_1 is always a fractional quantity. The result is that the hydrogen ion appears to move with a velocity much greater than its true characteristic velocity. Now let $U_{H\cdot}$ be the real velocity of the hydrogen ion. The total number of impacts with water molecules per second is $K_2N \cdot \pi \cdot S_1^2 U_{H\cdot} \cdot n$, where n is the

number of water molecules in a c.c. and S_1 the diameter of the hydrogen ion. The number of impacts attended with dissociation is $K_3 . K_2 . N . \pi . S_1^2 U_{H\cdot} . n$, and the distance saved per second $= K_1 . S . K_3 . K_2 . N . \pi . S_1^2 . U_{H\cdot} . n = C$ at a constant temperature, since K_1, K_2, K_3, $U_{H\cdot}$, have always the same value at constant temperature. C also does not vary with dilution if n and N do not vary. Now in the case of dilute solutions, the number of solvent molecules in a c.c. may always be regarded as constant, independent of concentration, without introducing much error. Since, according to the theory developed before, strong electrolytes are completely dissociated in dilute solutions, the number of hydrogen ions in a solution containing a gram-molecule is always constant. Whilst in the first process—the transference of electric charge by convection—only the free hydrogen ions take part, this is not the case in the second process. Here it stands more to reason to assume that all the hydrogen ions are equally efficient, for, considering that some of the hydrogen ions are stationary, there is nothing to prevent their collision with water molecules, for the latter are always free to move. In fact, the inactive hydrogen ions are always capable of vibratory motion. The distance C saved per second is thus independent of dilution.

Hence, for solutions of hydrochloric acid, on the basis that the activity-coefficient α at any dilution is the same as that of univalent binary salts, we get

$$\mu_v = \alpha(U_{H\cdot} + U_{Cl'}) + C_1 \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where α is the activity-coefficient at dilution v, and C_1 a constant independent of dilution. α can always be calculated from equation (1).

Again,

$$\mu_\infty = U_{H\cdot} + U_{Cl} + C_1 \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

From equations (3) and (4),

$$U_{H\cdot} = \frac{\mu_\infty - \mu_v - (1-\alpha)U_{Cl'}}{1-\alpha} \quad . \quad . \quad . \quad . \quad (5)$$

and

$$C_1 = \mu_\infty - U_{H\cdot} - U_{Cl'} \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

$U_{H\cdot}$, the real ionic mobility of the hydrogen ion, and C_1, the conductivity due to the second process, can thus at once be calculated from available data.

Experimental Confirmation of the above Hypothesis.—The experimental data on the conductivity of acids must always yield the same value of C_1 and $U_{H\cdot}$ provided the acid is a strong electrolyte. This expectation has been fully realised. Thus, for a solution of

hydrochloric acid at dilution 10 and temperature 25°, $\mu_v = 390{\cdot}4$, $\mu_\infty = 426$, $U_{Cl'} = 75{\cdot}8$, and $\alpha = 0{\cdot}844$, whence $U_{H\cdot} = 152{\cdot}4$ and $C_1 = 197{\cdot}8$.

Again, for solutions of nitric acid, at dilution 10, the available data give for $U_{H\cdot}$ 151·3 and 198·8 for C_1 (Noyes and Falk, *loc. cit.*). The values of $U_{H\cdot}$ and C_1 obtained from the data on the conductivity of hydrochloric and nitric acids therefore agree within 1 per cent. We may take 152 as the mean value of $U_{H\cdot}$ and 198·5 as that of C_1. The real mobility of hydrogen ion is therefore of the same order of magnitude as those of the other ions. The second process is thus responsible for the transference of about half the electric current in acid solutions.

The values of $U_{H\cdot}$ and C_1 having once been determined, it is possible to calculate the molecular conductivity of any strong acid at any dilution from equation (3). Tables III and IV show how the calculated values agree with the observed ones.

In table III, the observed values are taken from the work of Noyes and Falk (*loc. cit.*), whilst the data in table IV are obtained from a paper by Wegscheider and Lux (*Monatsh.*, 1909, **30**, 436).

TABLE III.

	$V =$	20.	100.	500.	1000.	2000.
HCl	μ_v calc.	397·6	408·9	416·5	418·4	—
	μ_v obs.	398·4	410·5	418·5	420·4	—
HNO_3	μ_v calc.	393·1	404·5	411·0	—	415·0
	μ_v obs.	393·3	406·0	413·0	—	417·0

TABLE IV.

	$V =$	100.	400.	111.	1600.
Naphthalene-β-sulphonic acid	μ_v calc.	637·2	372·4	375·3	376·3
	μ_v obs.	367·4	374·9	376·9	377·4
Toluene-*p*-sulphonic acid.....	μ_v calc.	369·9	375·0	377·6	378·5
	μ_v obs.	368·4	375·3	378·2	379·0

The agreement between the observed and calculated values is always within 0·5 per cent.

The real values of $U_{OH'}$ and C_1 for bases can also be obtained in the same way. Thus, at dilution 10, μ_v for potassium hydroxide is 213; μ_∞ is 240·2. From these data, the value of $U_{OH'}$ is 109 and of C_1 for bases 66. Table V shows how exactly the observed values of the molecular conductivity of potassium hydroxide agree with those calculated from equation (3).

TABLE V.

	$V=$	20.	50	100.	500.
KOH	μ_v calc.	218·4	224·0	227·1	232·5
	μ_v obs.	219·0	225·0	228·0	233·0

Arrhenius has already suggested "that the exceptionally great conductivity of these ions ($H^{\cdot}$ and OH') in water is probably due only to the fact that they are the two ions into which water is electrolytically decomposed" ("Theories of Solution," p. 138). In the foregoing pages, an attempt has been made to develop a quantitative explanation of the abnormal mobility of hydrogen and hydroxyl ions by assuming that an electric charge can be transferred almost instantaneously through water molecules during impact with these ions by the converse processes of dissociation and recombination taking place alternately.

A General Hypothesis for all Electrolytes.—The electrolytes can be classified into three groups, namely, (1) consisting of strong electrolytes, (2) containing acids of intermediate strength, "transition electrolytes," and (3) consisting of weak acids and bases where Ostwald's dilution law holds good.

For the first group we have the following empirical laws:

$\mu_v = \mu_\infty - a\sqrt[3]{C}$ (Kohlrausch, *Ann. Phys. Chem.*, 1885, [iii], **26**, 161) . . . . . (7)

and

$i = 2 - b - \sqrt[3]{C}$ (Noyes and Falk, *J. Amer. Chem. Soc.*, 1910, **32**, 101) . . . . . (8)

Equation (1) becomes identical with Kohlrausch's empirical law in the case of dilute solutions where μ_v is only slightly less than μ_∞. Thus, equation (1) may be put in the form

$$\frac{K}{\sqrt[3]{V}} = \log_e \frac{\mu_\infty}{\mu_v}$$

or

$$K\sqrt[3]{C} = \frac{\mu_\infty - \mu_v}{\mu_\infty} = 1 - \frac{\mu_v}{\mu_\infty} \quad . \quad . \quad . \quad . \quad (9)$$

or

$$\mu_v = \mu_\infty (1 - K \,.\, \sqrt[3]{C}) = \mu_\infty - a\sqrt[3]{C},$$

Again, the activity-coefficient

$$a = \frac{\mu_v}{\mu_\infty} = 1 - K\sqrt{C} \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

Noyes and Falk's empirical law can easily be derived by apply-

ing Clausius's virial theorem to salt solutions. It has already been shown that

$$i = n\left\{1 - \tfrac{1}{3}\log_e \frac{\mu_\alpha}{\mu_v}\right\} \quad . \quad . \quad . \quad . \quad . \quad (11)$$

$$= n\{1 - \tfrac{1}{3} K\sqrt{C}\}$$
$$= n - \tfrac{1}{3}n \,.\, K \,.\, \sqrt[3]{C}$$
$$= 2 - b\sqrt[3]{C}, \text{ for binary salts where } n = 2.$$

Whilst the strong electrolytes of group 1 belong to the limiting case, we have, for the other two groups, as in Arrhenius's original theory, both undissociated molecules and ions in solution. The law of mass action in its original form is, however, not applicable to electrically charged bodies. It requires modification in the sense that only the free ions take part in the equilibrium. It is only the fraction of the total number of ions which, by virtue of their kinetic energy, can overcome the force of electrostatic attraction, that really matter. They only are free to move, and hence have the chance of colliding with one another. From the kinetic point of view, therefore, only these free ions are to be taken into consideration in applying the law of mass action to the process of electrolytic dissociation. Thus, if x is the fraction of a gram-molecule of acid, which has undergone dissociation into ions, the law of mass action is not expressed by the equation

$$\frac{x^2}{(1-x)V} = K,$$

but by the equation

$$\frac{(\alpha x)^2}{(1-x)V} = K \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

where α is the activity-coefficient at the ionic concentration $\frac{x}{V}$. Now, α for any dilution can be calculated from equation (1) or (10). In the case of weak acids belonging to the third group, K is generally very small, $\frac{x}{V}$ becomes always negligibly small, and hence α is very nearly equal to one at all dilutions. For very weak acids, therefore, equation (12) becomes identical with Ostwald's dilution law.

A Dilution Formula for Transition Electrolytes.—Here the activity-coefficient α is not always equal to one, and the equation

$$\frac{(\alpha x)^2}{(1-x)V} = K,$$

must be applied as such. According to the ideas developed before,

the equivalent conductivity of an acid of intermediate strength may be equated thus:

$$\mu_v = x \,.\, 198{\cdot}5 + \alpha x(U_{H^\bullet} + U_{\text{Anion}}) \quad . \quad . \quad . \quad . \quad (13)$$

where x is the gram-equivalent of total hydrogen ion and $U_{H^\bullet} = 152$ at 25°, or

$$\mu_v = x \,.\, 198{\cdot}5 + (1 - K\sqrt[3]{C})x \,.\, (U_{H^\bullet} + U_{\text{Anion}}) \text{ from equation (10)}$$

$$= x(198{\cdot}5 + U_{H^\bullet} + U_{\text{Anion}}) - K\left(\frac{x}{V}\right)^{\frac{1}{3}} . x \,.\, (U_{H^\bullet} + U_{\text{Anion}})$$

$$\text{or since } c = \frac{x}{V}$$

$$= x \,.\, \mu_\infty - \frac{K}{\sqrt[3]{V}} . x^{\frac{1}{3}} . (U_{H^\bullet} + U_{\text{Anion}}).$$

The equation contains only one unknown quantity, x, and hence it admits of a solution. The real value of x can, however, be easily obtained with great accuracy by the method of successive approximation. x having thus been determined, it is easy to calculate α at concentration $\frac{x}{V}$. Hence all the factors for verifying the equation

$$\frac{(\alpha x)^2}{(1-x)V} = K,$$

can be had from the conductivity data. In tables VI, VII, VIII, and IX four acids have been chosen in the order of increasing strength to illustrate the validity of the above equation. The values of molecular conductivity have been taken from the very accurate work of Kendall (*loc. cit.*). According to this author, M for the hydrogen ion at 25° is 347, whilst the value obtained by Noyes and Falk as the mean of the data given by various workers is 350. In the following tables, the latter value has been accepted as true.

TABLE VI.

Cyanoacetic Acid. $\mu_\infty = 389{\cdot}1$ at 25°.

V.	μ_v.	x.	α.	K.
16·82	88·0	0·2370	0·9158	0·00365
33·64	117·0	0·3120	0·9260	0·00361
67·28	152·5	0·4050	0·9352	0·00358
134·56	193·9	0·5125	0·9442	0·00357
269·10	238·7	0·6283	0·9524	0·00358
538·20	282·6	0·7409	0·9606	0·00363
1076·40	320·0	0·8361	0·9673	0·00368

TABLE VII.

o-Nitrobenzoic Acid. $\mu_\infty = 382{\cdot}2$ at 25°.

V.	μ_v.	x.	α.	K.
32·0	139·7	0·3810	0·9204	0·00621
64·0	179·0	0·4854	0·9310	0·00620
128·0	221·9	0·5984	0·9407	0·00617
256·0	265·0	0·7106	0·9497	0·00616
512·0	303·6	0·8108	0·9588	0·00622
1024·0	333·5	0·8861	0·9664	0·00627

TABLE VIII.

Dichloroacetic Acid. $\mu_\infty = 388{\cdot}6$ at 25°.

V.	μ_v.	x.	α.	K.
16·0	231·4	0·6337	0·8835	0·0535
32·0	273·2	0·7400	0·9009	0·0534
64·0	309·8	0·8318	0·9174	0·0540
128·0	338·7	0·9020	0·9319	0·0550

TABLE IX.

Trichlorobutyric Acid. $\mu_\infty = 379{\cdot}0$ at 25°.

V.	μ_v.	x.	α.	K.
23·6	308·8	0·8616	0·8861	0·1783
47·2	331·7	0·9149	0·9068	0·1720
77·26	343·9	0·9434	0·9195	0·1720
108·0	350·4	0·9566	0·9273	0·1800

A comparison of the numbers in column five at once shows that for each acid a constant value of K is obtained. The degree of dissociation in the case of cyanoacetic acid has been varied from 0·23 to 0·83, but the equation holds good exactly throughout this interval.

The applicability of the formula has also been demonstrated for the entire range of transition electrolytes, beginning with cyanoacetic acid, which borders on the type of electrolytes included in the third group, and ending with trichlorobutyric acid, the strength of which is comparable with that of mineral acids.

Summary.

The abnormally high mobility of the hydrogen and hydroxyl ions in aqueous solutions has been explained on the assumption that electricity is partly carried by the ordinary process of convection and partly propagated through water molecules undergoing alternate dissociation and recombination. The apparently high activity-coefficients of strong acids and bases in aqueous solutions

has also been traced to this cause. A modified Ostwald equation, $\frac{(\alpha x)^2}{(1-x)V} = K$, based on the consideration that only free ions have the capacity of regenerating undissociated molecules, has been developed for weaker electrolytes, where the degree of dissociation is less than one. It has been shown that this equation becomes identical with Ostwald's dilution law in the case of very weak electrolytes where α is always very nearly equal to one, and also gives very concordant values for the equilibrium constant in the case of "transition electrolytes" where Ostwald's equation is not applicable.

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LXX.—*The Freezing Point Curve of Mixtures of Toluene-*o- *and* -p-*sulphonamides. Composition of Mixtures of Toluene-*o- *and* -p-*sulphonic Acids.*

By PHYLLIS VIOLET MCKIE.

AN accurate method of estimating the relative amounts of toluene-*o*- and -*p*-sulphonic acids in a mixture of the two acids can be based on the fusion curve of mixtures of the corresponding amides.

The composition of these acid mixtures has previously been investigated by Holleman (*Ber.*, 1911, **44**, 2504), by determining the freezing points of mixtures of the sulphonyl chlorides prepared from them. In this case, toluene-*m*-sulphonic acid was also generally present in small proportion. The freezing points of the *o*- and *p*-chlorides lie on a simple but rather flat eutectic curve. The eutectic point is not well defined, nor has it been directly determined by Holleman. From his figures, it would appear that this point lies in the neighbourhood of 1°, and that the eutectic mixture contains from 15 to 25 per cent. of the *p*-chloride.

The low range of temperature over which many of the mixtures of the *o*- and *p*-chlorides solidify (the *p*-chloride melts at 66·7° and the *o*-chloride at 10·0°, Holleman, *loc. cit.*), and the considerable manipulative difficulties encountered in preparing the mixture of chlorides in a state in which the fusion point can be observed (*loc. cit.*), constitute objections to the use of this method for the purpose

of determining the composition of mixtures of the toluene-*o*- and -*p*-sulphonic acids.

These difficulties are lessened or disappear if the mixture of crude acid chlorides is converted into amides, a transformation which can be very simply and quantitatively carried out. Moreover, it is necessary only to dry the amide mixture before determining the fusion point, whereas the mixture of acid chlorides must finally be distilled under diminished pressure. The melting points of the mixtures of amides lie in a very convenient range of temperature, namely, 110—156°, and, as will be seen from the curve, the eutectic point is extremely sharply defined. The eutectic mixture contains 61·25 per cent. of the *p*-sulphonamide, and melts at 110·25°.

Preparation of Materials.—The toluenesulphonic acid, or mixture of acids, is converted into the sulphonyl chloride by treatment with phosphorus pentachloride and phosphoryl chloride (Polak, *Rec. trav. chim.*, 1910, **29**, 416; compare Holleman, *loc. cit.*), and the sulphonyl chlorides are extracted with ether from the product of the reaction after it has been treated with ice. After some of the ether has been evaporated, solid ammonium carbonate, and finally some alcoholic ammonia, is added, the mixture being gently warmed by placing it at intervals on a water-bath. The reaction is known to be complete when the very penetrating odour of the sulphonyl chloride has disappeared. The conversion may also be conveniently effected by grinding the mixture in a mortar.

The product of amidation, after the evaporation of solvents, is extracted with as little cold water as possible to remove ammonium salts, and then dried at 100° to expel the water of crystallisation of the *p*-amide.

The *p*-amide separates from aqueous solution with two molecules of water. The dihydrate melts, if heated rapidly, at 105°, but is best rendered anhydrous by drying at 100°:

0·1730 when dried at 100—110° for two hours lost 0·0282.

$H_2O = 16{\cdot}3$.

$C_7H_9O_2NS,2H_2O$ requires $H_2O = 17{\cdot}3$ per cent.

Both the *o*- and *p*-amides can be purified and almost completely freed from the isomeride by careful crystallisation from water. Final purification was effected by sublimation in the vacuum of a Töpler pump, which raised the melting point by a few tenths of a degree. Resublimation of material which had been thus treated produced no further change.

The melting point of toluene-*p*-sulphonamide is given as 137° (Klason and Vallin, *Ber.*, 1873, **12**, 1853), and that of toluene-*o*-

sulphonamide as 153—154° (Wolkow, *Zeitsch. für Chem.*, 1870, 327) and 155° (Noyes, *Amer. Chem. J.*, 1886, **8**, 176). After sublimation in a vacuum, the latter melts at 156·3° and the former at 137·45°.

Determination of the Fusion Points.—Holleman recommends a special form of heating-bath (*loc. cit.*), by means of which stirring is avoided. In the present work, the following arrangement was employed: The heating-bath is a beaker containing clear, colourless glycerol, and is fitted with a stirrer. The material is placed in a small tube, fitted with a thermometer reading to 0·1° and a stirrer. This tube is enclosed in a larger tube, so that an air-space prevents direct contact with the glycerol. Sufficient material is taken to ensure that the bulb of the thermometer is completely covered by the molten mass. With the thermometer and the tube which were used, 0·5—1·5 grams were required. The whole apparatus was carefully screened from draughts.

The heat was supplied by a small hooded gas-jet, regulated by a screw clip compressing the rubber tubing. No difficulty was experienced in keeping the temperature of the bath constant over considerable periods. When determining a melting point, the temperature of the bath was raised to within a degree or so of the expected fusion point *before* introducing the jacketed tube containing the material. Prolonged heating and sublimation were thus avoided. The inner tube with its fittings—thermometer and stirrer—and containing the material, was weighed before and after a determination in order to check any loss through sublimation. The maximum loss observed in any case amounted only to 0·0004 gram on a total weight—tube, thermometer, material, etc.—of 10 grams.

The temperature of the bath is gradually raised until incipient fusion is observed. At no time was the temperature of the heating-bath more than 1° above that registered by the thermometer in the material. The melting point is taken as the temperature at which the material liquefies, save for one or two crystals. On maintaining the thermometer steady for ten to fifteen minutes, the crystals should not disappear. On raising the temperature 0·1°, they should melt.

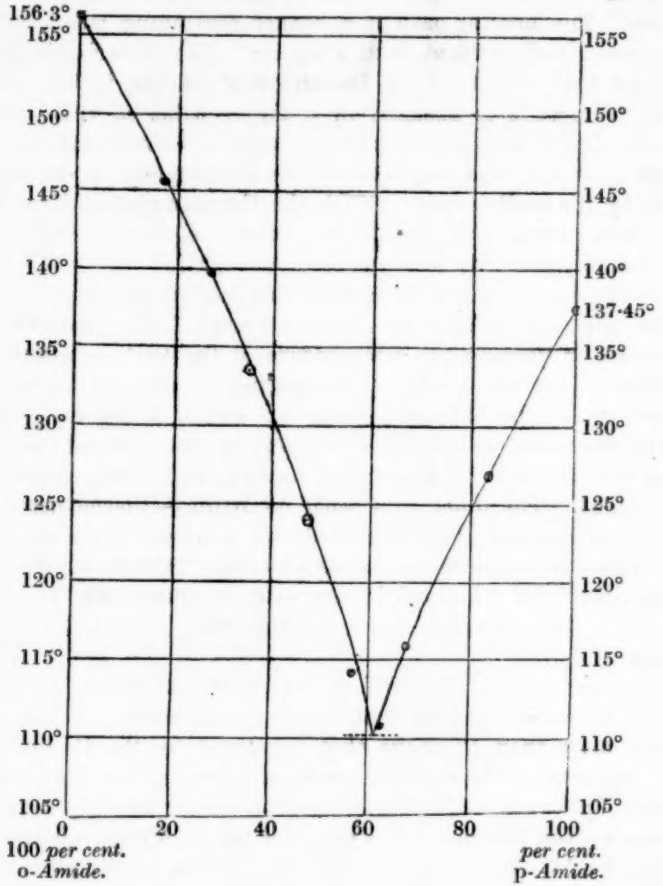
In the case of the pure substances, the variation of the thermometer from the point of incipient fusion to complete melting did not extend to more than 0·5°.

*Toluene-*p*-sulphonamide.*—Middle fraction of the sublimate obtained by sublimation in vacuum.

(1) Incipient fusion, 137°; bath, 138° for ten minutes. All but

one crystal melted, 137·40°; bath, 138° for fourteen minutes. Last crystal melted, 137·5°.

(2) The temperature was kept at 137·45° for five minutes; all but one crystal melted. This melted on raising the temperature to 137·5°, bath 138°. The melting point of toluene-*p*-sulphonamide is therefore taken as 137·45°.



Toluene-o-sulphonamide.—The crude material has an average melting point of 148—152°. One recrystallisation from water raises the melting point to 154—155°. On further recrystallisation, the melting point is raised to 156°. Material which had been recrystallised from water was sublimed in a vacuum. As in the former case, all but the middle fraction was neglected.

(1) Incipient fusion, 156·1°; bath, 157° for ten minutes. All

but one crystal melted, 156·3°; bath, 157° for ten minutes. Last crystal melted, 156·4°.

(2) The external temperature was maintained at 156·7° for twenty minutes, the temperature of the inner thermometer registering 156·3°. A trace of solid remained, which melted on raising the temperature to 156·4°. The melting point of toluene-*o*-sulphonamide is therefore taken as 156·3°.

Plotting of the Curve.—The melting point of a weighed portion of one of the components was determined. Successive weighed portions of the other pure component were then added, and the melting point was determined for each mixture. The curve was followed, starting from both the pure ortho- and the pure para-compound. When the curve had been plotted in this way, single points on it were determined, separate mixtures being made up for each determination.

o-Amide. Gram.	*p*-Amide. Gram.	*p*-Amide. Per cent.	Melting point.
0·3241	0	0	156·3°
0·3241	0·0709	17·96	145·5
0·3958	0·1381	25·87	139·7
0·3235	0·1787	35·58	133·6
0·3958	0·2698	40·54	130·3
0·3235	0·2839	46·74	124·0
0·3958	0·4020	50·39	120·8
0·2478	0·3267	56·87	114·1
0·3958	0·6230	61·15	110·4
0·3958	0·8200	67·45	115·9
0·1212	0·5752	82·59	126·8
0·2839	0·0	100·0	137·45

I wish to express my thanks to Professor Orton, at whose suggestion and under whose direction this work has been carried out, for his guidance and criticism.

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LXXI.—*The Compound* $H_2B_4O_6$ *and its Salts.*

By RAMES CHANDRA RAY.

IN a previous communication (T., 1914, **105**, 2162), it was shown that the so-called amorphous boron, prepared by the reduction of boron trioxide by means of magnesium, probably consisted of a solid solution of a lower oxide of boron, sometimes in combination with a little magnesium oxide, in elementary boron. If this were

really the case, it appeared probable that the soluble part of the fusion would contain some of the lower oxide, together with excess of boron trioxide, and the present investigation was undertaken with a view to detect and isolate the lower oxide.

The fusion obtained by heating a mixture of boron trioxide with magnesium powder generally contains magnesium boride, amorphous boron (so-called), magnesium oxide, partly in combination with boron trioxide, and, as will be shown later, the lower oxide or oxides of boron. If the operation is carried out under conditions which will now be described, the quantity of magnesium boride in the mixture is very small, although it cannot be altogether eliminated.

A mixture of 1 part of magnesium powder and 3·5 parts of anhydrous boron trioxide, finely powdered and passed through a 120-mesh sieve, was heated in a covered magnesia-lined crubible, through which a current of hydrogen was passed, to a bright red heat for about three hours. After cooling in an atmosphere of hydrogen, the mass was powdered and mixed with half its weight of anhydrous boron trioxide. The mixture was then heated again as before. The fused mass was powdered, water was added to it, and it was allowed to remain for from one to three days, to allow of the decomposition of traces of magnesium boride.

The solution was filtered, and the boric acid removed by the method employed by Travers, Ray, and Gupta (*Pamphlet*, H. K. Lewis and Co., 1916), which consisted in shaking the solution in a vacuum for several days with precipitated magnesium hydroxide, and removing the excess of the latter, together with the insoluble magnesium metaborate, by filtration In analysing the solutions, advantage was also taken of the fact, discovered by Travers, Ray, and Gupta (*loc. cit.*), that when solutions of the lower oxides of boron are evaporated with excess of lime and the residue ignited to constant weight, oxidation does not take place and the increase in the weight of the lime corresponds with the weight of the lower oxide in the solution. For the purpose of analysis, three equal quantities of the solution were treated as follows:

(*a*) The magnesium was precipitated in the usual manner and the result expressed as the oxide MgO.

(*b*) The solution was introduced into a platinum crucible containing lime, ignited to constant weight, and, after evaporation to dryness, the crucible was again ignited to constant weight, the increase in weight giving the weight of the magnesium oxide and of the lower oxide of boron, together with the weight of any trace of boric acid left in the solution.

(c) The third portion of the solution was evaporated to dryness in a vacuum and the residue heated in a sealed bulb with concentrated nitric acid. The bulb became filled with red fumes, and the lower oxide of boron was oxidised to boron trioxide. The bulb was then opened, the excess of nitric acid removed by evaporation in a vacuum desiccator over solid sodium hydroxide, and the boric acid determined by the lime method.

The following are the results of the experiments:

	I.	II.	III.	IV.	V.
MgO per 100 c.c. of solution	0·0980	0·1156	0·1248	0·0876	0·1608
Residue less MgO per 100 c.c.	0·3048	0·3584	0·3896	0·2726	0·5012
B_2O_3 from residue per 100 c.c.	0·3452	0·4036	0·4324	0·3048	0·5664
MgO in gram-mols. per 100 c.c.	0·0024	0·0029	0·0031	0·0022	0·0040
B in gram-atoms per 100 c.c.	0·0099	0·0115	0·0123	0·0087	0·0161
Ratio B/Mg	4·1	3·9	4·1	3·9	4·0
$\frac{B_2O_3}{\text{(Residue less MgO)}}$	1·132	1·126	1·112	1·118	1·130

It is clear that the ratio B/Mg is very near 4, and that the mean value of the ratio B_2O_3/(Residue less MgO), which is 1·124, closely approximates to the value of the ratio $2B_2O_3/B_4O_5$, which is 1·129. The analytical results appear, therefore, to suggest that the solution contains a magnesium borite, the formula of which may be written MgO,B_4O_5. The oxide B_4O_5 has already been described by Travers, Ray, and Gupta (*loc. cit.*).

Each of the solutions used in these experiments was obtained from the treatment of a different fusion, and it was possible, therefore, although hardly probable, that the constancy of their composition might be attributable to the fact that the conditions in each case were similar. The third preparation was therefore treated with water four times, and the extracts were investigated separately. The results of the analysis of the first extract have already been given; those of the remaining extracts are tabulated below:

	III, *a*.	III, *b*.	III, *c*.
MgO per 100 c.c.	0·0960	0·0616	0·0412
Residue less MgO per 100 c.c.	0·2940	0·1804	0·1212
B_2O_3 from residue per 100 c.c.	0·3290	0·1996	0·1368
MgO in gram-mols.	0·0024	0·0015	0·0010
B in gram-atoms	0·0094	0·0057	0·0039
Ration B/Mg	3·9	3·8	3·9
$\frac{B_2O_3}{\text{(Residue less MgO)}}$	1·119	1·106	1·128

Although the solutions became more and more dilute with each treatment of the fusion with water, their composition remained

practically constant, leaving no room for doubt that the compound MgO,B_4O_5 is really present in them.

It has not been found possible to isolate the magnesium borite.

The molecular weight of the compound can be determined with sufficient accuracy from the freezing points of the solutions. If the magnesium salt were completely dissociated, the molecular weight of the corresponding oxide could be determined from the formula

$$\Delta = 18{\cdot}5(W/M + W'/40),$$

where W is the weight, in 100 c.c. of the solution, of the oxide of boron, M its molecular weight, and W' the weight of the magnesium oxide present. Since, however, the compound is probably dissociated only to the extent of about 75 per cent., the result will be about 15 per cent. too high.

For the determination of the freezing points, measured quantities of the solutions, of which the analyses have already been given, were evaporated to dryness in a vacuum. The residues were dissolved in a measured quantity of water, and the freezing points were compared with the freezing point of pure water. The following results were obtained:

	I.	II.	III.	IV.	V.
W	0·3048	0·3584	0·3896	0·2726	0·5012
W'	0·0980	0·1156	0·1248	0·0876	0·1608
Δ	0·090	0·105	0·115	0·082	0·148
M	121	128	125	124	125
Ratio B_4O_5/MgO	1·0	0·95	1·0	1·0	1·0

The values for M agree sufficiently well with the theoretical value, 124, as calculated for the formula B_4O_5.

On addition of ammonia to the solution, the magnesium is almost completely precipitated as hydroxide, and if the ammoniacal solution is evaporated in a vacuum, a residue is left which consists mainly of the oxide. As Travers, Ray, and Gupta have shown (*loc. cit.*), the oxide is very unstable and is readily oxidised to boric acid.

If a solution of the magnesium salt is treated with potassium hydroxide in equivalent proportions, and afterwards evaporated in a vacuum to small bulk, practically the whole of the magnesium separates as hydroxide and can be filtered off. On further concentration of the solution in a vacuum, the potassium salt separates as a crust which can be redissolved, and the salt purified by crystallisation five or six times, and finally dried in a vacuum at 80—90°. The preparation is a difficult one, and altogether only 2 to 3 grams

of the substance were finally obtained. The salt is stable in the absence of moisture.

The potassium was estimated by first dissolving the salt in water, evaporating the solution to dryness in a platinum vessel, and treating the residue repeatedly with hydrochloric acid and methyl alcohol. The potassium chloride was finally converted into sulphate. For the estimation of boric acid, the solution was saturated with carbon dioxide and boiled under a reflux condenser in a current of pure air. The boric acid was titrated with $N/20$-alkali in the presence of mannitol, using phenolphthalein as indicator:

I. 0·5036 gave 0·3987 K_2SO_4 and 0·3142 B_2O_3. K = 35·5; B = 19·6.

II. 0·2286 gave 0·1821 K_2SO_4 and 0·1433 B_2O_3. K = 35·7; B = 19·7.

III. 0·3678 gave 0·2889 K_2SO_4 and 0·2318 B_2O_3. K = 35·2; B = 19·8.

$K_2B_4O_6$ requires K = 35·8; B = 20·2 per cent.

The analyses are concordant, and the results in agreement with the values corresponding with the formula $K_2B_4O_6$, which may therefore be accepted as correct.

The molecular weight of the substance was determined by the cryoscopic method, using 20 grams of solvent:

0·0435 gave $\Delta^t = -0·052$. M.W. = 78.

0·0874 „ $\Delta^t - 0·097$. M.W. = 84.

The value of the molecular weight calculated for the formula $K_2B_4O_6$ is 218, and if the compound were completely dissociated in solution, the apparent molecular weight would be 73. The concentrations of the two solutions correspond with 1 gram-equivalent in 100 and 50 litres respectively, and if the salt is ionised to the same extent as similar potassium salts, the degree of ionisation in the two solutions will be approximately 0·9 and 0·8. Without going further into the matter, it is obvious that, within the limits of experimental error, the result proves that the substance in solution has the formula $K_2B_4O_6$, and not the formula KB_2O_3, which would dissociate into two ions and give an apparent molecular weight of approximately 50.

The existence of the anhydrous salt, $K_2B_4O_6$, of the acid $H_2B_4O_6$ is of interest, as it goes to confirm the views put forward by Travers, Ray, and Gupta (*loc. cit.*) as to the constitution of the borohydrates containing four atoms of boron. If the boron atoms in these compounds are linked in a single chain, the oxide, B_4O_5,

which can be obtained by heating them, must be given the formula $BO{:}BO{\cdot}BO{:}BO$ (with a bridging O), and the corresponding acid the formula

$$BO(OH){:}BO{\cdot}BO{:}BO(OH).$$

The results do not offer any positive evidence that the so-called amorphous boron is a solid solution of the oxide B_4O_5 in elementary boron, particularly as Travers, Ray, and Gupta have found indications of the existence of the oxide B_2O, which is quite insoluble in water, and may be the oxide that is present in the solid solution. The research has, however, led to the discovery of a new series of compounds, the acid, $H_2B_4O_6$, and its salts, and the results serve to extend our knowledge of the more complex compounds of boron.

In conclusion, I desire to thank Dr. M. W. Travers, F.R.S., at whose suggestion the research was undertaken, for the valuable help which I have always received from him.

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LXXII.—*The Hydrates and Alcoholate of Calcium Benzoate.*

By FREDERICK STANBRIDGE.

THE investigations recorded in this paper were suggested by a chance observation by Dr. C. F. Baker of the action of alcohol on calcium benzoate. This salt, in its usual form, is a crystalline trihydrate having the formula $Ca(C_6H_5{\cdot}CO_2)_2{,}3H_2O$. When heated on the water-bath, it loses part of its water, and it was noticed that when this partly dehydrated substance was covered with alcohol, a distinct change in appearance took place, the substance becoming flocculent.

Close examination under the microscope of the action of alcohol on the trihydrate showed the presence, a minute after adding the alcohol, of nuclei on each crystal from which, as centres, bundles of new, needle-shaped crystals grew with great rapidity. Similar results were obtained in tests made under the microscope on the completely dehydrated salt, obtained by heating the trihydrate in an air-oven, in which the original crystalline shape was retained in spite of the loss of water.

These observations point to the formation of a compound of calcium benzoate and alcohol, formed from the anhydrous substance by the simple addition of alcohol, and from the trihydrate by the substitution of alcohol for the water of crystallisation. This compound was prepared and analysed.

The calcium benzoate was prepared specially from pure benzoic acid and pure precipitated calcium carbonate by the usual method. The average yield of the trihydrate from 40 grams of benzoic acid was: first crop, 34 grams; second crop, 11 grams; third crop, 4 grams, a total of 49 grams, representing 89 per cent. of the theoretical yield, which is 55·1 grams. The purity of the salt was checked by estimations of the water and of the calcium. (Found: $H_2O = 15{\cdot}80$, $15{\cdot}74$; $Ca = 14{\cdot}15$, $14{\cdot}12$. Calc.: $H_2O = 16{\cdot}08$; $Ca = 14{\cdot}21$ per cent.)

The new compound was prepared by first dehydrating 10 grams of the trihydrate in the air-oven at about 150°, allowing to cool, and then adding 30 c.c. of alcohol specially dried by distillation from quicklime. The mixture became warm and set to a soft mass. It was allowed to remain for a day, being stirred a few times to break up lumps. The excess of alcohol was removed by filtration, and the solid product pressed between filter-paper. After drying in the air, analysis showed that the substance had reverted almost completely to the trihydrate. (Found: $H_2O = 15{\cdot}99$ per cent.) In order to ensure drying, and yet to prevent the elimination of combined alcohol, it was found satisfactory to place the product over a mixture of anhydrous calcium chloride and alcohol for four days.

The dried material is a light, white powder having a strong odour of alcohol. Under the microscope, it was seen to consist of very small, transparent needles which, on the addition of a drop of water, clotted together in semi-opaque masses, with needle-shaped crystals projecting from their boundaries. On gently heating a small portion of the substance in a test-tube, alcohol was given off copiously, and this condensed to liquid in the upper, cooler part of the tube. With sodium carbonate and iodine solutions the substance gave the iodoform reaction for alcohol.

In order to determine the exact proportions of alcohol and water in combination in the product, the matter volatile up to 150° was estimated by combustion. A sample was weighed in a small U-tube, and then this was half immersed in a beaker of sulphuric acid provided with a thermometer and stirrer. The temperature of the bath was raised to 150°, while a stream of pure and dry air was passed through the U-tube and thence through a combustion tube filled with copper oxide and heated in a furnace. The

water and carbon dioxide were absorbed and weighed as usual, and from the weights of these the quantities of water and alcohol in the sample were calculated. Analyses at intervals gave the following results, after correction by a blank experiment:

Time after placing over calcium chloride and alcohol.	Water, per cent.	Alcohol, per cent.
4 days	0·51	24·36
5 „	0·11	24·68
7 „	2·03	24·46
17 „	—	24·02
494 „	2·03	21·61
$Ca(C_6H_5\cdot CO_2)_2,2C_2H_6O$ requires	0	24·61

The results leave no doubt that the substance is a dialcoholate of calcium benzoate, having the formula $Ca(C_6H_5\cdot CO_2)_2,2C_2H_6O$. Calcium benzoate thus shows a property which is shared by a number of other salts of calcium, of taking up alcohol to form an unstable additive compound.

The next question that presented itself was, What happens when the trihydrate is treated with alcohol? As alcohol is hygroscopic, it should extract water from the trihydrate, but whether a lower hydrate, the anhydrous salt, or the alcoholate is to be expected as the result cannot be stated without further investigation as to the compounds possible and the conditions under which these are stable.

Rough experiments, made by adding different mixtures of alcohol and water to the trihydrate, to ascertain between what limits of composition action took place at the ordinary temperature, showed that a mixture containing 95 per cent. of alcohol by volume had no action, whilst one containing 97 per cent. acted rapidly.

Attempts to determine by a dilatometer the temperature at which a given mixture of alcohol and water just begins to act on the trihydrate met with no success, but using the thermometric method with the same mixture of alcohol and water ($D^{15\cdot6}$ 0·8149, corresponding with 92·85 per cent. of alcohol by weight), a marked change was observed to take place at 35·5°, the trihydrate being transformed into silky, oblong plates. After separating these and drying them over a mixture of calcium chloride and alcohol for one to two days, analyses were carried out in the same way as in the case of the alcoholate:

Found: $H_2O=6\cdot43$, $6\cdot42$; $C_2H_6O=0$.

$Ca(C_6H_5\cdot CO_2)_2,H_2O$ requires $H_2O=6\cdot00$ per cent.

The new substance is therefore the monohydrate formed from the trihydrate by the extraction of 2 molecules of water of crystallisation by the mixture of alcohol and water.

Since another hydrate of calcium benzoate besides the ordinary one had thus been found, it was decided to make a study of calcium benzoate by itself to see what possible substances might be formed by the action of alcohol on the trihydrate.

In order to search for transition points, a dilatometer was first used, containing trihydrate and anhydrous substance and filled with amyl alcohol in one set of experiments, and containing trihydrate and monohydrate and filled with toluene in another set. Beyond slight evidence of a transition point below 90° in the second set of experiments, no very definite results were obtained.

The measurement of the solubility of the trihydrate at various temperatures was adopted finally as the best method. The apparatus used was similar to that described by Lumsden (T., 1902, **81**, 350), employing, however, a hot-air motor for stirring the thermostat tank, an electro-motor for stirring the mixture of crystals and water, and a mercury thermo-regulator of the Ostwald pattern. A gas-pressure regulator of the form *A* described by Stansfield (*Trans. Faraday Soc.*, 1911, **7**, 116) was employed, by which the temperature in the thermostat tank could be kept constant within 0·1° quite easily, even at the highest temperature, 97°, at which the tank was used. After placing the solubility apparatus in position in the tank, the mixture of crystals and water was stirred for periods varying from $4\frac{1}{4}$ to $12\frac{1}{4}$ hours. The mixture was then filtered into a receiver while the whole apparatus was still immersed. At first a small flask was used as receiver, and from this about 10 c.c. of the solution were transferred to a weighed platinum crucible for analysis. For determinations at 80° and upwards, the flask was replaced by a weighing bottle, into which the solution was filtered directly in order to obviate, as far as possible, loss of water by evaporation during the transference of the hot solution, and, after weighing, the solution was poured into a platinum basin for analysis. This apparatus and procedure sufficed for temperatures from about 20° up to 97°. For 10°, the temperature of the tank was adjusted by passing a stream of ice-cold water through the zig-zag tube provided for the purpose on the bottom of the tank. For 0°, the same saturation and filtration apparatus was immersed in clean, chopped ice. For determinations at the boiling point of the saturated solution, at first the Beckmann ebullioscopic apparatus was employed. Excess of the powdered crystals was boiled with distilled water in the apparatus for about three hours, and the temperature and barometric height were noted. Some of the solution was then drawn by suction into a weighing bottle through a tube to the lower end of which was attached a small glass bulb filled with cotton wool in order to

retain any solid. The sample was weighed and transferred to a platinum basin for analysis. The boiling point of pure water was determined in the same apparatus under the same conditions, the barometric height being again noted. From the latter observation, the correction to be added to the observed temperature of the boiling solution to get the true temperature was obtained, and from this the elevation of the boiling point of the saturated solution above that of pure water. Later it was found simpler to boil excess of the powdered crystals with water in an ordinary boiling tube with a layer of beads at the bottom and with a small reflux condenser at the top, the barometric height during the course of the experiment being noted. The temperature of the boiling solution was obtained indirectly by adding to the boiling point of pure water at the observed pressure, as given by tables, the mean elevation of the boiling point by saturation with the crystals as determined by the first experiments with the Beckmann apparatus.

In all cases, in order to estimate the strength of the saturated solution, this was evaporated to dryness, the residue repeatedly treated with concentrated sulphuric acid and ignited, and the calcium weighed as calcium sulphate.

When 90° was passed, results were obtained which appeared anomalous, but this was soon found to be due to the existence of a transition point between 80° and 90°. Special care was taken in this interval of temperature, and the solubility was measured at about 83°, 85°, 87°, and 89°, whereby it was ascertained that the transition point is near 85°, and that the solubility curve above this temperature is distinct from that below. It was possible to obtain points on the metastable portions of both curves near 85° which enabled them to be plotted, and therefore the transition point to be ascertained with greater accuracy. The change from the hydrate stable at the lower temperatures to that stable at the higher temperatures is so sluggish at 90° that three of the ordinary solubility determinations, lasting for seven or eight hours, for which the mixture of crystals and water was heated to 90°, but not above, gave points on the curve for lower temperatures. For the same reason, to get the points for 85°, 87°, 89°, 91°, and 93° on the curve for higher temperatures, it was found necessary to heat the mixture to 98° before the period of saturation. To obtain results for 83° on the metastable portion of the curve for higher temperatures, it was found satisfactory to mix calcium benzoate, completely dehydrated, with a hot solution saturated at the boiling point, and to cut down the time of mixing and stirring at 83° to about two hours.

All results which were not obviously untrustworthy are collected

in table I. Each was obtained from a separate complete experiment, unless indicated otherwise by brackets. The temperatures have been corrected, and are probably true to 0·1°. The solubility is expressed as grams of anhydrous calcium benzoate per 100 grams of water. The hydrate that is in contact with the saturated solution is denoted by the figure I for that stable at lower temperatures and II for that stable at higher temperatures.

TABLE I.

Temperature.	Solubility.	Hydrate.		Temperature.	Solubility.	Hydrate.
0·2°	2·235	I		84·9°	7·652	II
0·2	2·229	,,		87·0	7·702	,,
0·2	2·232	,,		87·0	7·705	,,
9·8	2·454	,,		87·0	7·718	,,
9·8	2·452	,,		89·1	7·832	,,
19·9	2·720	,,		89·1	7·870	,,
19·9	2·726	,,		89·1	7·848	,,
19·9	2·722	,,		89·1	7·852	,,
29·8	3·016	,,		90·3	8·614	I metastable
30·1	3·026	,,		90·2	8·529	,, ,,
39·7	3·426	,,		90·2	8·523	,, ,,
39·7	3·421	,,		91·1	8·040	II
39·7	3·426	,,		91·1	7·949	,,
49·7	4·070	,,		91·1	8·026	,,
49·7	4·032	,,		93·2	8·237	,,
49·7	4·056	,,		93·1	8·198	,,
49·7	4·036	,,		93·2	8·087	,,
59·8	4·719	,,		93·1	8·095	,,
59·8	4·699	,,		95·2	8·349	,,
59·8	4·708	,,		95·2	8·371	,,
69·7	5·630	,,		95·2	8·424	,,
69·9	5·618	,,		95·2	8·371	,,
69·7	5·710	,,		97·2	8·450	,,
70·0	5·769	,,		97·2	8·453	,,
70·0	5·650	,,		97·2	8·539	,,
79·6	6·857	,,		97·2	8·513	,,
79·9	6·865	,,	Boiling point	100·2	8·800	,,
82·9	7·561	II metastable		99·6	8·537	,,
82·9	7·502	,, ,,		100·0	8·455	,,
82·9	7·518	,, ,,		99·4	8·610	,,
82·9	7·528	,, ,,		99·5	8·766	,,
84·9	7·614	II		100·6	8·880	,,
85·0	7·563	,,		100·4	8·814	,,

Many efforts were made to obtain specimens of the solid hydrate stable in contact with saturated solution above the transition point. The first method used was that described by Lumsden (*loc. cit.*), the apparatus employed being similar to that figured by him. No results of any value were obtained; the solid product was a fine white powder, and consequently retained a considerable quantity of saturated solution. By the second method, two small quantities of the trihydrate were heated in separate small bulbs in communication with one another to temperatures above the

transition point, but one somewhat higher than the other, whereby the water in the saturated solution formed in the first was made to distil gently over into the second until no further loss of weight of the first bulb and contents could be detected. In two experiments of this kind there was a loss of 30·22 grams and 30·48 grams of water per gram-molecule of the trihydrate in the hotter bulb, suggesting the formation of the monohydrate, for which the loss of weight per gram-molecule of the trihydrate would be 36 grams.

It appeared desirable to complete the study of the equilibrium of solutions of calcium benzoate in water by determining the freezing-point curve of solutions of various strengths. The measurements of the freezing points were carried out in the usual manner with the Beckmann apparatus. The experiments were made in two series, in the first of which successive quantities of powdered trihydrate were added to a given quantity of water in the apparatus, whereas in the second a stock solution of calcium benzoate was made, slightly more concentrated than the solution saturated at 0°, and the freezing points of this and of solutions consisting of 80, 60, 40, and 20 c.c. of the stock solution diluted to 100 c.c. with water, were determined. The results of the two series of experiments are given in table II.

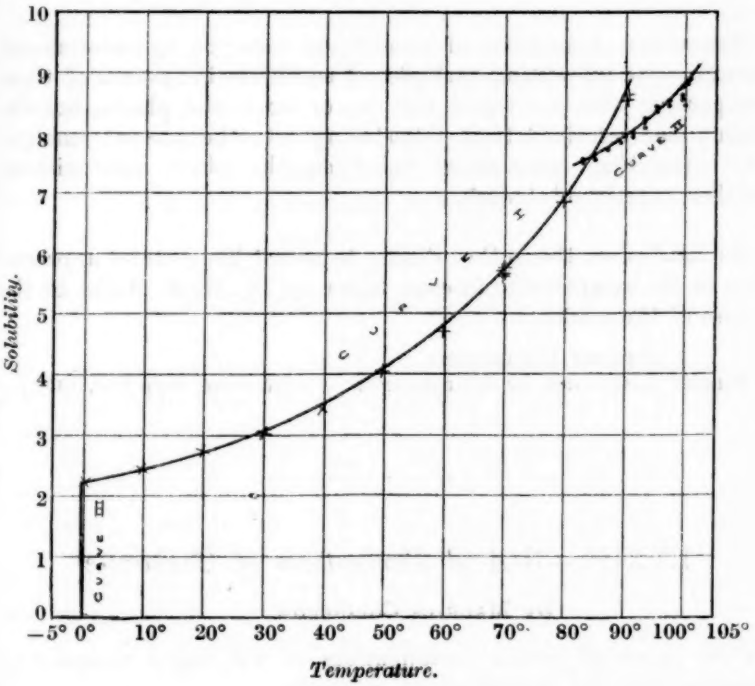
TABLE II.

1st Series.		2nd Series.	
Grams of $Ca(C_6H_5 \cdot CO_2)_2$ per 100 grams of water.	Freezing point.	Grams of $Ca(C_6H_5 \cdot CO_2)_2$ per 100 grams of water.	Freezing point.
0	0°	0	0°
0·3098	−0·100	0·4473	−0·129
0·7680	−0·220	0·8964	−0·159
1·421	−0·308	1·347	−0·282
1·760	−0·370	1·801	−0·289
—	—	2·263	−0·382
—	—	3·470	−0·369

The mean graphs for the two sets of determinations do not coincide very nearly, but by taking points midway between them along the ordinates, it is possible to make, for a given quantity of calcium benzoate in solution, an approximation to the freezing point correct to about 0·01°. The cryohydric point was about −0·37°.

The results in tables I and II are shown in the diagram, which represents completely the stable equilibrium between calcium benzoate and its solutions at all temperatures between the cryohydric point and the boiling point of the saturated solution. The

solubility curve consists of two distinct portions, the one (I) for the lower temperatures defining equilibrium between the trihydrate and saturated solution, the other (II) for the higher temperatures defining that between a lower hydrate and saturated solution. The two curves cross at 84·7°, corresponding with a concentration of 7·62 grams of calcium benzoate per 100 grams of water, and this is therefore the transition point. Curve III is the freezing-point curve, and the concentration at the cryohydric point −0·37°, obtained by extrapolation of curves I and III, is



2·22 grams of calcium benzoate per 100 grams of water. As regards the solid phases, that corresponding with curve I is undoubtedly the trihydrate. Although it has not been possible to isolate from the saturated solution that corresponding with curve II, there is reason for supposing it to be the monohydrate, $Ca(C_6H_5{\cdot}CO_2)_2,H_2O$.

Summary.

Anhydrous calcium benzoate combines with alcohol to form a dialcoholate, $Ca(C_6H_5{\cdot}CO_2)_2,2C_2H_6O$, which is very unstable.

Mixtures of alcohol and water containing much alcohol extract

water from the crystalline trihydrate, $Ca(C_6H_5\cdot CO_2)_2,3H_2O$, to form a monohydrate, $Ca(C_6H_5\cdot CO_2)_2,H_2O$.

A study of the solubility of the trihydrate at various temperatures shows that a lower hydrate exists, the transition temperature being 84·7° and the solubility 7·62 grams of calcium benzoate per 100 grams of water. This lower hydrate is probably the monohydrate, $Ca(C_6H_5\cdot CO_2)_2,H_2O$.

A study of the freezing points of solutions of calcium benzoate shows that the cryohydric point is −0·37°, when the solution contains 2·22 grams of calcium benzoate per 100 grams of water.

The action of mixtures of alcohol and water on hydrates should furnish some interesting examples of equilibria in systems of three components with one liquid and two or more solid phases, but the author has refrained from introducing into the present example any theoretical speculations based on the phase rule without further experimental work.

In conclusion, the author desires to record his grateful appreciation of the sympathetic interest taken by Dr. C. F. Baker in the course of the work.

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LXXIII.—N-*Acyl Derivatives of Carbazole.*

By MAURICE COPISAROW.

IN the course of certain investigations, it was found necessary to prepare *N*(9)-acyl derivatives of carbazole.

As but few substances of this class are known,* it was decided to investigate this subject further, this being the more desirable, as the known methods of preparation are not satisfactory.

The drawbacks of the methods so far employed are: (1) The necessity of heating the acid chloride or anhydride with carbazole

* *N*-Acetylcarbazole (Graebe and Glaser, *Annalen*, 1872, **163**, 351; Böeseken, *Rec. trav. chim.*, 1912, **31**, 164), carbazole-*N*-carboxylic acid (Ciamician and Silber, *Gazzetta*, 1882, **12**, 272; Oddo, *ibid.*, 1911, **41**, I., 255), *N*-benzoylcarbazole (Bizzarri, *ibid.*, 1890, **20**, 413; Mazzara, *Ber.*, 1891, **24**, 279), and carbazole-*N*-carbonyl-*o*-benzoic acid (Stümmer, *Monatsh.*, 1907, **28**, 411).

to a comparatively high temperature before the reaction takes place, the product being impure and the yield low; (2) the employment of condensing agents, such as sulphuric acid, ferric chloride (Böeseken, *loc. cit.*), and aluminium chloride (Stümmer, *loc. cit.*; Scholl and Neovius, *Ber.*, 1911, **44**, 1249), which may cause the formation of *C*-acyl derivatives of carbazole (Borsche and Feise, *Ber.*, 1907, **40**, 378); and (3) the constitution of the carbazole derivatives so formed is established only in an indirect or negative manner.

The author has found that by adopting in this case a method analogous to that generally employed in the preparation of *N*-alkyl derivatives of carbazole, namely, condensing the acid haloids, usually the chlorides, with potassium carbazole, good results are obtained.

The general mechanism of formation of the *N*-acyl derivatives of carbazole can be represented by the following equations:

$$C_{12}H_8NK + R{\cdot}COCl = C_{12}H_8N{\cdot}COR + KCl, \text{ and}$$
(I.)

$$2C_{12}H_8NK + R\langle\begin{matrix}COCl\\COCl\end{matrix} = C_{12}H_8N{\cdot}CO{\cdot}R{\cdot}CO{\cdot}NH_8C_{12} + 2KCl.$$
(II.)

It was observed that the energy of reaction and the stability of the products decrease with the complexity of the acyl group in the case of monobasic acids.

It has also been noted that in the case of the *C*- and *N*-acyl derivatives of carbazole, their solubility and fusibility diminish with the increase in the number of carbazole groups in the molecular structure of the product (Stümmer, *loc. cit.*; Scholl and Neovius, *loc. cit.*; Ehrenreich, *Monatsh.*, 1911, **32**, 1102; Copisarow and Weizmann, T., 1915, **107**, 878).

The *N*-acyl derivatives of carbazole investigated by the author give colourless solutions in concentrated sulphuric acid, these solutions assuming a deep green coloration on the addition of a few drops of concentrated nitric acid, the only exception being *N*-oxalylcarbazole. This is probably due to the greater stability of oxalylcarbazole, on the one hand, and the comparative ease with which the derivatives containing one carbazole group in their molecule are hydrolysed, regenerating carbazole, on the other. So far as the experimental evidence goes, *N*-oxalylcarbazole cannot be regarded as an intermediate product in the formation of "carbazole-blue," prepared by the fusion of carbazole with oxalic acid (Suida, *Ber.*, 1879, **12**, 1403; Bamberger and Müller, *ibid.*, 1887, **20**, 1903).

Experimental.

The general method of preparation of the *N*-acyl derivatives of carbazole adopted by the author was to triturate potassium carbazole, prepared by Graebe's process (*Annalen*, 1880, **202**, 28), with a slight excess of the acid chloride; the reaction being energetic, the addition of the latter is regulated accordingly. The mixture is allowed to remain for two hours, then extracted successively with water, dilute sodium carbonate, and water again, so as to remove the potassium chloride and acidic substances, and then dried.

On triturating potassium carbazole with acetyl and benzoyl chlorides, there were obtained the *N*-acetyl and *N*-benzoyl derivatives of carbazole respectively, in the forms described by previous workers (*loc. cit.*).

The following compounds are further examples of the general reaction.

N-*Phenoxyacetylcarbazole*, $\begin{matrix}C_6H_4\\C_6H_4\end{matrix}\!>\!N\cdot CO\cdot CH_2\cdot OPh.$

The product of the interaction of potassium carbazole and phenoxyacetyl chloride, a pale grey powder, is soluble in all the ordinary organic solvents. It crystallises from ethyl alcohol (after decolorising the solution with animal charcoal) in white, slender needles decomposing at 121—122°, with the regeneration of carbazole.

The colourless solution of *N*-phenoxyacetylcarbazole in concentrated sulphuric acid gives with nitric acid the deep green coloration characteristic of carbazole:

0·3854 gave 15·16 c.c. N_2 at 18° and 763 mm. N = 4·59.

$C_{20}H_{15}O_2N$ requires N = 4·62 per cent.

N-n-*Nonoylcarbazole*, $\begin{matrix}C_6H_4\\C_6H_4\end{matrix}\!>\!N\cdot CO\cdot [CH_2]_7\cdot CH_3.$

The product of the reaction of potassium carbazole with *n*-nonoyl chloride is readily soluble in the usual organic solvents. It crystallised from ethyl alcohol in long, prismatic needles melting at 72—73°:

0·3266 gave 12·4 c.c. N_2 at 17° and 762 mm. N = 4·42.

$C_{21}H_{25}ON$ requires N = 4·56 per cent.

On heating *N*-*n*-nonoylcarbazole above its melting point, the acyl group is eliminated, decomposition also taking place on attempting to crystallise the substance from a solvent of high boiling point.

N-*Palmitylcarbazole*, $\begin{matrix}C_6H_4\\C_6H_4\end{matrix}\!>\!N\cdot CO\cdot[CH_2]_{14}\cdot CH_3$.

The reaction between potassium carbazole and palmityl chloride, being less energetic than those described above, is completed by keeping the mixture in an air-oven at 75° for two hours, the mixture being triturated from time to time.

The product, a grey powder, is readily soluble in all the ordinary organic solvents. The difference in solubility in hot and in cold ethyl alcohol is considerable, and the compound crystallises from this solvent in a spongy mass of small, white, matted needles melting at 90—91°. It separates from benzene in small, rhombic crystals:

0·4603 gave 12·4 c.c. N_2 at 18° and 763 mm. N = 3·12.

$C_{28}H_{39}ON$ requires N = 3·45 per cent.

On being heated above its melting point, the compound decomposes, carbazole being regenerated.

N-*Carbonylcarbazole*, $\begin{matrix}C_6H_4\\C_6H_4\end{matrix}\!>\!N\cdot CO\cdot N\!<\!\begin{matrix}C_6H_4\\C_6H_4\end{matrix}$.

Dry carbonyl chloride was passed over finely powdered potassium carbazole, the current of gas being so regulated as to keep the temperature of the energetic reaction at 150—160°. When the reaction ceased, the product, freed from potassium chloride and acidic substances, was crystallised from ethyl alcohol, the first crop of crystals being mainly unchanged carbazole. After three crystallisations, the compound was obtained in small, white needles melting at 181—183°:

0·2805 gave 19 c.c. N_2 at 16° and 760 mm. N = 7·92.

$C_{25}H_{16}ON_2$ requires N = 7·78 per cent.

N-*Carbonylcarbazole* is more readily soluble than carbazole in the ordinary organic solvents.

Paschkowetzky's (*Ber.*, 1891, **24**, 2905) failure to prepare N-carbonylcarbazole by boiling potassium carbazole with carbonyl chloride in benzene solution was probably due to the low temperature. Even in boiling xylene no condensation takes place, although the reaction appears to be energetic.

N-*Oxalylcarbazole*, $\begin{matrix}C_6H_4\\C_6H_4\end{matrix}\!>\!N\cdot CO\cdot CO\cdot N\!<\!\begin{matrix}C_6H_4\\C_6H_4\end{matrix}$.

The reaction between potassium carbazole and oxalyl chloride is energetic, and the operation was carried out in a manner similar

to that adopted in the case of monobasic acid derivatives of carbazole. Under these conditions, no acid of the type $>N\cdot CO\cdot CO_2H$ was formed. The crude product, freed from potassium chloride and oxalic acid, was extracted with hot alcohol to remove any unaltered carbazole. The pale grey powder is very sparingly soluble in alcohol, ether, light petroleum, chloroform, or pyridine, but somewhat more readily so in ethyl acetate, acetic acid, benzene, nitrobenzene, acetone, or carbon disulphide, and crystallises from nitrobenzene or carbon disulphide in small, white, rhombic crystals melting at 265—266°:

0·2360 gave 14·56 c.c. N_2 at 17° and 762 mm. N = 7·18.
$C_{26}H_{16}O_2N_2$ requires N = 7·21 per cent.

N-Oxalylcarbazole does not give with concentrated nitric acid in the presence of concentrated sulphuric acid the deep green coloration characteristic of carbazole and many of its derivatives.

It appeared to be of interest to investigate whether this substance is an intermediate product in the formation of "carbazole-blue" from carbazole and oxalic acid. To determine this, the following experiments were carried out: (1) The product of the reaction between oxalyl chloride and potassium carbazole was heated to above 200°; (2) the product of the reaction between oxalyl chloride and carbazole was heated to above 200°; and (3) oxalylcarbazole was fused with a large excess of oxalic acid and the mixture heated to above 200°.

In all these cases, no formation of "carbazole-blue" could be detected, and therefore *N*-oxalylcarbazole cannot be regarded as an intermediate product in the formation of "carbazole-blue."

The author wishes to express his indebtedness to the Department of Industrial and Scientific Research for permission to publish this work.

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LXXIV.—*The Relative Activity of certain Alkyl Iodides with Sodium α-Naphthoxide in Methyl Alcohol.*

By Henry Edward Cox.

The relative activities of methyl, ethyl, and *n*-propyl iodides with sodium naphthoxides in ethyl alcohol were discussed in a previous paper (this vol., p. 666), and attention was directed to the abnormal increase in activity of methyl iodide at high dilutions. The object of the present work was to examine similarly the reaction between methyl iodide and sodium α-naphthoxide in methyl alcohol as solvent.

Menschutkin (*Zeitsch. physikal. Chem.*, 1890, **6**, 41) found that ethyl iodide and triethylamine react more rapidly in methyl alcohol than in ethyl alcohol, and ascribed this to the higher dielectric constant of the methyl alcohol. Hecht and Conrad (*ibid.*, 1889, **3**, 42) and Segaller (T., 1914, **105**, 112) have shown that sodium ethoxide and phenoxide react more rapidly in ethyl alcohol as solvent. This is surprising in view of the fact that Robertson and Acree (*Amer. Chem. J.*, 1913, **49**, 474; T., 1914, **105**, 2582) have shown that in the case of the phenoxide, the activity due to ions is more than five times that due to the undissociated phenoxide. The activity would therefore be expected to be higher in the solvent of greater dissociating power, namely, methyl alcohol. Sodium α-naphthoxide, like ethoxide and phenoxide, reacts about twice as fast with the alkyl iodides in ethyl alcohol as in methyl alcohol.

Experimental.

The methyl alcohol was quite free from acetone, and was dehydrated over calcium oxide and calcium. The measurements were carried out at 40·0°, as described in the previous paper.

The following results were obtained with methyl iodide and sodium α-naphthoxide in equivalent concentration. The third column gives the values of k_v calculated from the equation $k_v = k_1 + a \log v$.

$a = 0{\cdot}00333$.

v.	k_v (found).	k_v (calc.).
1	0·01644	0·01644
2	0·01797	0·01744
4	0·01863	0·01844
8	0·01923	0·01945
16	0·02449	0·02045
32	0·03633	0·02145
64	0·04461	0·02245

These figures show that the above equation holds as far as $v=8$, and then k_v increases abnormally rapidly, as was found to be the case in ethyl alcohol.

In order to determine whether the increase with dilution is mainly due to the change in concentration of the naphthoxide or of the methyl iodide, the following experiments were made with non-equivalent concentrations. The results are calculated from the usual formula, $k=\frac{1}{(a-b)t}\log_e\frac{b(a-x)}{a(b-x)}$, where a and b are the concentrations of iodide and naphthoxide respectively.

The results show that change in concentration of the alkyl iodide has comparatively little effect on the velocity constant, whereas the concentration of the naphthoxide has a very marked effect.

		k.
N/16-Naphthoxide;	*N*/4-Methyl iodide	0·02243
	N/8- „ „	0·02321
	N/16- „ „	0·02449
N/8-Iodide	*N*/8-Naphthoxide	0·01923
	N/16- „	0·02321
N/4-Iodide	*N*/4-Naphthoxide	0·01863
	N/16- „	0·02449

On plotting values of k against $\log v$, there is a sharp curve upwards at the point corresponding with about $v=8$. It seemed possible that at higher dilutions the reaction might not be bimolecular, but of a higher order, due to the formation of additive compounds, such as $C_{10}H_7\cdot ONa, xCH_3I$, and in order to test this point, Ostwald's 'isolation' method was applied, as follows.

The reaction velocity may be represented by the equation $-dc_1/dt=kc_1^mc_2^n$, where c_1 and c_2 are concentrations of naphthoxide and iodide respectively. In the following experiments, c_2 is large compared with c_1, and is taken as constant during that part of the reaction measured; the equation then takes the form $-dc_1/dt=k_1c_1^m$, where $k_1=kc_2^n$. The order of reaction is then equal to m.

Experiment I.
N/16-Naphthoxide.
N/1-Iodide.

t.	c.	$1/t\log c_0/c$.
0	6·45	—
30	3·70	0·00804
55	2·35	0·00797
65	2·00	0·00786
75	1·62	0·00800

Mean $k_1'=0·00797$

Experiment II.
N/16-Naphthoxide.
N/4-Iodide.

t.	c.	$1/t\log c_0/c$.
0	7·30	—
66	5·10	0·00236
83	4·75	0·00225
106	4·20	0·00226
148	3·50	0·00217

Mean $k_1''=0·00224$

Experiment III.
N/16-Naphthoxide.
N/8-Iodide.

t.	c.	$1/t\log c_0/c$.
0	7·60	—
77	6·10	0·00124
96	5·80	0·00122
130	5·35	0·00117
160	4·95	0·00116

Mean $k_1'''=0·00120$

The values of k_1 are sufficiently constant to show that the reaction is unimolecular with regard to the naphthoxide.

If k_1' and k_1'' are values of k_1 from two experiments in which the concentration of naphthoxide is initially the same, whilst that of the methyl iodide is varied and equal to c_2' and c_2'', then $k_1' = kc'_2{}^n$ and $k_1'' = kc''_2{}^n$, hence $n = \log \frac{'}{k_1''} \Big/ \log \frac{c_2'}{c_2''}$. Substituting the values obtained in experiments I, II, and III, $n = 0{\cdot}92$, $0{\cdot}91$, $0{\cdot}90$, which indicates that n approaches the value unity. The reaction is therefore unimolecular with respect to methyl iodide, and the whole reaction is bimolecular at all dilutions from $N/1$ to $N/64$.

Effect of the Products of Reaction on the Velocity Coefficient.

Arrhenius, and more recently Senter, have pointed out that velocity coefficients often exhibit a tendency to fall off as the experiment proceeds, owing to the action of the salts formed during the reaction. As the constants in the reactions here considered show this tendency to diminish, the following experiments were made with an addition of anhydrous sodium iodide and α-naphthyl methyl ether respectively.

	k.
$N/8$-Sodium α-naphthoxide and $N/8$-methyl iodide.	
No sodium iodide	0·01923
$N/4$ „ „	0·01929
$N/8$ „ „	0·01907
$N/8$ α-Naphthyl methyl ether	0·01690
$N/4$-Naphthoxide and $N/4$-methyl iodide.	
No α-Naphthyl methyl ether	0·01865
$N/4$- „ „ „	0·01535

These results show that whilst sodium iodide has no appreciable influence on the velocity coefficient, the formation of the ether greatly retards the velocity, and this probably accounts for the observed falling off of the velocity constant.

It is still unexplained why the velocity is practically constant throughout any one experiment, although the concentration falls to less than one-half of its initial value, whereas if an experiment is commenced at a lower concentration, the velocity coefficient is considerably increased in accordance with the equation $k_v = k_1 + a \log v$.

Ethyl and n-*Propyl Iodides.*

These iodides react more slowly than methyl iodide, and the equation $k_v = k_1 + a \log v$ is found to hold to as high a dilution as it was practicable to measure.

The results of three experiments are as follows:

	Ethyl iodide.		*n*-Propyl iodide.	
v.	k_v (found).	k_v (calc.).	k_v (found).	k_v (calc.).
1	0·005350	0·005350	0·002355	0·002355
8	0·006026	0·005982	0·003071	0·003077
32	0·006280	0·006403	0·003601	0·003559
	$a=0·00070$		$a=0·00080$	

The relative activities of the three iodides at concentration $N/1$ are:

Solvent :—	Methyl alcohol.	Ethyl alcohol.
Methyl iodide	6·98	9·55
Ethyl iodide	2·27	2·14
n-Propyl iodide	1·00	1·00

and the ratio of the velocity coefficients in these two solvents is:

	Methyl iodide.	Ethyl iodide.	*n*-Propyl iodide.
Methyl alcohol ...	1·00	1·00	1·00
Ethyl alcohol.....	2·50	1·71	1·83

These figures agree very closely with the results of Hecht and Conrad and of Segaller for sodium ethoxide and phenoxide.

Summary and Conclusions.

(1) The reaction between methyl iodide and sodium α-naphthoxide is bimolecular at all dilutions from $N/1$ to $N/64$. The velocity coefficient increases with dilution in accordance with the equation $k_v=k_1+a\log v$ as far as $v=8$, and thereafter it increases more rapidly.

(2) The effect of varying the concentration of the alkyl iodide is comparatively small, but the initial concentration of the naphthoxide has a very marked effect on the velocity coefficient.

(3) Sodium iodide has no effect on the velocity coefficient.

(4) α-Naphthyl methyl ether greatly retards the reaction.

(5) The velocity of reaction of the alkyl iodides is approximately twice as great in ethyl alcohol as in methyl alcohol.

(6) The relative activity of the first three members of the series is in the order methyl, ethyl, *n*-propyl iodide, and methyl iodide is much more active than the others.

I wish to express my thanks to Mr. G. R. Thompson for providing every facility for this work, and to Dr. J. C. Crocker for his interest and advice.

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LXXV.—*The Hydrolysis of Soap Solutions, Measured by the Rate of Catalysis of Nitrosotriacetonamine.*

By JAMES WILLIAM MCBAIN and THOMAS ROBERT BOLAM.

THE concentration of hydroxyl ion in soap solutions was measured by McBain and Martin (T., 1914, **105**, 957) by the electromotive force method, and the measurements recorded in the present paper agree with those results in showing that the concentration of hydroxyl ion is only of the order of magnitude of $N/1000$. It is therefore impossible to attribute the conductivity of soap solutions to free hydroxyl ions. For the evidence with regard to the existence and nature of the ionic micelle and their bearing on the conductivity, reference should be made to other communications from this laboratory.*

Method of Measurement.

The method employed was the rate of catalysis of the reaction

$$CO\langle\begin{matrix}CH_2\cdot CMe_2\\CH_2\cdot CMe_2\end{matrix}\rangle N\cdot NO \longrightarrow H_2O + N_2 + CO\langle\begin{matrix}CH{:}CMe_2\\CH{:}CMe_2\end{matrix},$$

as shown by Francis and his collaborators (T., 1912, **101**, 2358; 1913, **103**, 1722; 1915, **107**, 1651). The reaction is unimolecular and the velocity is proportional to the concentration of hydroxyl ion. The volume method had been found to be accurate to within about 2 or 3 per cent. at the ordinary temperature.

The results are calculated according to the system proposed by McBain (*Trans. Faraday Soc.*, 1917, **13**, 1), which consists in always setting the rate constant equal to unity and in choosing the unit of time accordingly.

The formula used here is consequently

$$T = 2{\cdot}303 \log \frac{A}{A-x},$$

instead of the hitherto customary

$$k = \frac{2{\cdot}303}{t} \log \frac{A}{A-x}$$

where k is the rate constant. The disadvantages of the system hitherto employed, as compared with that proposed, are illustrated

* McBain and Taylor, *Ber.*, 1910, **43**, 321; *Zeitsch. physikal. Chem.* 1911, **76**, 179; Bowden, T., 1911, **99**, 191; McBain, Cornish, and Bowden, T., 1912, **101**, 2042; Bunbury and Martin, T., 1914, **105**, 417; McBain and Martin, T., 1914, **105**, 957; Laing, T., 1918, **113**, 435; McBain and Salmon, *J. Amer. Chem. Soc.*, 1918; McBain, *J. Soc. Chem. Ind.*, 1918, **37**, 249 (a brief summary).

by the rate of reaction in the presence of 0·0138*N*-OH' at 40·0°. The rate constant is 0·0708. This statement is meaningless until the further information is given that "time has been measured in minutes." Under the new system, this becomes—"the time unit is 14·1 minutes"—a statement which is much more readily visualised, is self-contained, and does away with small decimals. It further means, in the case of unimolecular reactions such as the present, that the reaction requires 14·1 minutes to proceed to the extent of 63·2 per cent.

Determinations were made at 30°, 40°, 70°, and 90°. The values of the time units for definite concentrations of hydroxyl ion at each temperature were measured by observing the rate in solutions of sodium hydroxide. These solutions were made up from sodium and boiled-out conductivity water, and all vessels were carefully flushed out with air freed from carbon dioxide. Soap solutions were made up in silver vessels as described in previous communications. The reaction was carried out in a Jena-glass flask containing a small glass tube, which could be dropped into the solution in the flask when it was desired that the reaction should commence. In some cases this tube contained the soap solution, in others the solution of nitrosotriacetonamine. 0·1300 Gram of that substance was employed in each case. The amount of gas which should have been evolved, saturated with water vapour at about 18°, is 17·18 c.c.; as a matter of fact, on the average about 8 per cent. more than this was evolved. Francis and Clibbens state that they obtained values within 2·5 per cent. of the theoretical volume. Hence the "infinity reading" was taken after a period five times as long as that required for the production of 9·3 c.c. of nitrogen.

The results for sodium hydroxide are given in table I, in the final column of which the product of "time unit" and concentration is recorded. This should be a constant for each temperature, and is also equal to the reciprocal of the older expression k/OH'. The final products for 40°, 70°, and 90° are 0·196, 0·0236, and 0·00545, respectively. The degree of accuracy is much less at the higher temperatures, owing to the great speed of the reaction and the very low concentrations of hydroxyl ion, which alone are measurable. Further, the solubility of the glass and difficulties due to vaporisation and fluctuations of temperature play an increasing rôle. However, none of these influences vitally affects the value of the results, on account of the fact that the hydrolysis of the soaps is itself so small.

TABLE I.

Rate of Catalysis in Solution of Sodium Hydroxide.

Temperature.	Concentrations. $NaOH_{18}$.	Concentrations. $OH'=C.$	Number of experiments.	Time units T minutes. Max.	Min.	Mean.	C.T.
40°	0·0146	0·0139	4	14·4	13·5	14·1	0·196
70	0·00314	0·00302	4	8·32	6·80	7·67	0·0232
,,	0·00392	0·00396	2	6·52	6·45	6·49	0·0244
90	0·000654	0·000626	2	9·43	9·01	9·22	0·00579
,,	0·000785	0·000757	2	7·69	7·46	7·57	0·00569
,,	0·000796	0·000766	2	6·41	6·33	6·37	0·00488

The temperature coefficient of the reaction above 40° is 2·02 and 2·04, depending on whether the time unit at 70° or 90° is taken for the calculation. This is in general agreement with the results previously and subsequently obtained (T., 1915, **107**, 1657), showing that the temperature coefficient diminishes with rise of temperature.

Applicability of the Method.

In view of the low values of hydroxyl ion obtained for soap solutions, it was considered advisable to carry out a few experiments in order to determine the neutral salt action, if any, of the sodium salt by the lowest fatty acid of this series, namely, sodium acetate.

The results of two series of experiments are given in table II, where concentrations are expressed in volume normality at 90°. The first column gives the preparation used (*A* being sodium acetate made anhydrous by heating in an air-bath at 125°, *C* and *D* being ordinary crystals weighed either dry or moist after recrystallisation and subsequently analysed, thus avoiding any slight loss of acetic acid through heating), the last column being the apparent hydroxyl-ion concentrations as deduced from the factors obtained from table I.

TABLE II.

Sodium Acetate at 90° *with and without Sodium Hydroxide.*

NaAc.	Concentrations. NaAc.	Concentrations. NaOH.	Number of experiments.	Time units minutes. Max.	Min.	Mean.	$(OH')_v$.
D, *C*	0·923	—	2	28·1	25·5	26·8	0·000203
A	0·967	—	2	25·0	24·4	24·7	0·000221
C, *D*	0·923	0·000759	3	10·4	9·0	9·81	0·000556
A	0·967	0·000759	2	9·7	8·9	9·32	0·000585

These results require elucidation, for there are two factors involved, namely, neutral salt action and hydrolytic equilibrium. Taking first hydrolysis, calculation shows that the observed rate of catalysis would indicate a rather high value, $60—70 \times 10^{-14}$, for K_w, the dissociation constant of water at 90°. The latter is still uncertain as between the limits $33—70 \times 10^{-14}$. With the present method, dilute solutions would have to be employed to minimise neutral salt action.

The nature of the neutral salt action follows from the experiments in table II, employing added sodium hydroxide. The sodium hydroxide added will, of course, be only moderately dissociated in accordance with the principle of isohydrism. The total rate predicted will consequently be less than that of the hydroxide when taken alone, in spite of the influence of hydrolysis. Taking one set of assumptions in the preceding paragraph, the hydroxyl ion predicted is about 0·000614 for both the 0·923 and 0·967*N*-solutions containing sodium hydroxide. Taking another set, using osmotic data, this number becomes about 0·000571, which is identical with the mean of the observed value in table II.

This suffices to show that sodium acetate in normal solution does not exhibit any accelerating neutral salt effect. If it has any effect, it retards the reaction by anything up to 6 per cent., which is within the experimental error for the calculation above.

A much more vital effect would be if the soap in concentrated solutions sorbs nitrosotriacetonamine, thus cutting down the effective concentration at any time, and therefore the rate. The reaction would proceed to completion, for the whole of the amine would be liberated progressively, but the apparent rate would be proportionately less than that corresponding with the real concentration of hydroxyl ion. The whole of the nitrogen is actually evolved.

If this phenomenon occurs, it would be of importance only in concentrated solutions, where the soaps exist as colloidal electrolytes. There the apparent concentration of hydroxyl ion would be too small, whereas in dilute solutions, in which the soaps exist essentially as simple electrolytes, normal values would be observed.

This is just what is found when the results from the present method are compared with those from the determination of electromotive force (*loc. cit.*). The values are nearly identical up to *N*/20-solution, but at N/10-solution they begin gradually to diverge until at 0·8*N*-solution the alkalinity measured by catalysis is only a fraction of that found by the method of electromotive force.

The only uncertainty in the measurements from electromotive

force is in calculating the diffusion potential. If the difference between the methods is to be ascribed to this source, it would make the hydrolysis much smaller even than that deduced, which was one or two tenths of a per cent. This establishes even more conclusively the main result of the previous paper. This assumption, however, predicates that the palmitate micelle possesses only low equivalent mobility, whereas the high observed conductivity necessitates the opposition conclusion. If sorption is taken into account, the results obtained by the catalytic method confirm those derived from electromotive force.

Direct proof of the occurrence of sorption in concentrated solution is obtained by adding a known amount of sodium hydroxide to the soap and observing that the effect on the rate is abnormally low. This is not due to sorption of the hydroxyl ion by the soap, as both electromotive force data (*loc. cit.*) and other evidence show that basic soaps are not formed. Experiments of this kind are set forth in table III. The concentrations of sodium palmitate are given in weight normality, the sodium hydroxide in volume normality at 90°. Two experiments from table I are added for comparison. The results show strikingly that the apparent rate is much lower than that corresponding with the alkali present and added, which points to sorption of amine by soap in concentrated solution as the explanation of the low rate. It should be remembered, of course, that in these soap solutions the concentration of sodium ions is about 0·30 weight normal, or about 0·25 volume normal at 90°, so that the sodium hydroxide is not fully dissociated and the hydrolysis of the soap has been partly repressed. Even so, the observed rate is but a fraction of that expected.

The last three lines of table III present experiments carried out by J. C. Pope in June, 1918, using a special preparation of sodium palmitate, which, although discoloured, was found to be very slightly alkaline in 90 per cent. alcoholic solution. The rate in mixtures containing considerable excess of alkali is about six times less than if the soap had been absent. This confirms the conclusions already drawn and reconciles the results of the catalytic and electromotive force methods set forth in table IV.

TABLE III.

0·8 *Sodium Palmitate at* 90° *with and without Sodium Hydroxide.*

Concentration.		Number of experiments.	Time units minutes.			(OH').
NaP.	NaOH.		Max.	Min.	Mean.	Deduced.
0·8	—	3	25·0	19·9	21·6	0·000252
„	0·000774	3	20·7	18·9	19·8	0·000275
—	0·000785	2	7·69	7·46	7·57	0·000784
1·0	—	2	15·0	14·8	14·9	0·000266
„	0·00374	1	—	—	8·09	0·000614
„	0·0187	1	—	—	1·75	0·00312

Results with Soap Solutions.

Measurements on solutions of pure palmitate have been carried out at 30°, 40°, 70°, and 90°. The results for sodium palmitate are given in table IV, and those for potassium palmitate in table V.

TABLE IV.

Alkalinity of Solutions of Sodium Palmitate.

Temperature.	Concentration: weight normality.	Number of experiments.	Time units minutes.			$(OH')_v$.	Hydrolysis, per cent.	By E.M.F., per cent.
			Max.	Min.	Mean.			
70°	0·046	4	43·7	42·0	42·8	0·000438	0·99	—
„	0·101	2	43·5	42·6	42·0	0·000561	0·59	—
90	0·042	2	6·02	5·98	6·0	0·000908	2·24	2·3
„	0·50	2	27·0	27·0	27·0	0·000202	0·05	0·37
„	0·8	3	25·0	19·9	21·6	0·000252	0·04	0·28

TABLE V.

Alkalinity of Solutions of Potassium Palmitate.

Temperature.	Concentration: weight normality.	Number of experiments.	Time units minutes.			$(OH')_v$.	Hydrolysis, per cent.	by E.M.F., per cent.
			Max.	Min.	Mean.			
30°	0·050	2	561·6	520·6	541·1	0·00097*	2·04	—
40	0·051	2	598·8	431·0	514·9	0·000391	0·82	—
70	0·050	3	43·7	42·6	43·1	0·000545	1·14	—
„	0·100	2	38·8	38·3	38·5	0·000612	0·65	—
„	0·85	4	409·9	380·2	395·1	0·0000594	0·009	—
90	0·019	3	7·4	7·0	7·2	0·000757	4·1	5·7
„	0·042	2	6·06	5·7	5·9	0·000928	2·3	2·2
„	0·1	4	6·1	5·7	5·9	0·000927	0·99	1·25
„	0·302	5	12·7	6·1	9·4	0·000580	0·22	0·64
„	0·85	1	—	—	49·5	0·000110	0·017	0·27

* These experiments were carried out by F. H. Geake by the pressure method. As the solutions have begun to be heterogeneous the alkalinity is, as expected, greater than at the higher temperatures where it is liquid. Compare McBain and Martin, *loc. cit.*, p. 975.

The seventh column gives the concentration of hydroxyl ion deduced, neglecting the effect of sorption of amine, and in the eighth the percentage hydrolysis found by electromotive force measurements (*loc. cit.*) is added for comparison.

Comparison of the last two columns in tables IV and V brings out the agreement of the two methods for dilute solutions, whilst the divergence in the concentrated solution is due to sorption of amine by the colloidal soap, as already explained.

The tables show at once that the alkalinity of all soap solutions is low and cannot account for more than a few per cent. of the conductivity of soaps except in very dilute solutions. However, it is quite sufficient to exclude the existence of free palmitic acid in soap solutions except in very minute amount (see McBain and Martin, *loc. cit.*, p. 973). Since the concentration of the hydroxyl ion exceeds $0{\cdot}00002N$ in the case of every soap solution, even when containing excess of fatty acid, all higher fatty acids which are formed or added must exist in the form of acid soap, that is, in solid solution, adsorbed or chemically combined, but not in the free condition, except to an immeasurably small extent. This combats a very prevalent error (see, for instance, Washburn, "Principles of Physical Chemistry," 1915, p. 379).

Potassium palmitate when studied by the method of electromotive force exhibits a maximum alkalinity equal to $0{\cdot}000316N$ in $0{\cdot}5N$-solution, diminishing to a quarter of this value in $1{\cdot}00N$-solution, which corresponds with only 0·08 per cent. hydrolysis. The data for sodium palmitate were less definite, but it was shown (*loc. cit.*, p. 973) that the values in concentrated solution tend to be too high. This effect also helps to explain the divergence between the two methods in concentrated solutions. The falling off in absolute alkalinity is quite simply explained on the basis of McBain and Salmon's theory of colloidal electrolytes (*J. Amer. Chem. Soc.*, 1918), for in concentrated solutions the palmitate ions largely disappear, being displaced by the ionic micelle.

A word is necessary with regard to what we have called "hydrolysis, per cent.," in the last two columns of tables IV and V, for which we have been criticised by Bancroft (*Trans. Amer. Electrochem. Soc.*, 1915, **27**, 184). Bancroft's criticism arises from our having regarded alkalinity (concentration of hydroxyl ion) as hydrolysis. The difference is largely a matter of words and of point of view. His contention is that the hydrolysis may have been anything up to 100 per cent., but that the hydroxyl ion has been immediately and almost quantitatively sorbed by the resulting acid palmitate (it cannot be palmitic acid, and the colloidal sodium palmitate must contain all the excess of palmitic acid liberated).

McBain and Martin's paper contains direct measurements of the alkalinity of sodium hydroxide in the presence of soap; the hydroxide shows no appreciable sorption by soap; this is direct experimental evidence which has apparently not been considered by Bancroft, and would appear to be conclusive.

Summary.

Rate of catalysis, like electromotive force, shows that soap solutions are definitely, although very slightly, alkaline.

This alkalinity decreases with falling temperature, but is increased again when the solution solidifies or becomes heterogeneous.

The concentration of hydroxyl ion observed in all cases is sufficient to exclude the widely held view of the possibility of the existence of appreciable amounts of free fatty acid in any soap solution. Instead, acid soap must be formed in which practically all the excess of fatty acid is sorbed or combined.

The experiments here communicated are taken from a series that had to be discontinued in July, 1914. Our thanks are due to the Colston Society of the University of Bristol for a grant which has defrayed the expenses of this investigation.

CHEMICAL DEPARTMENT,
BRISTOL UNIVERSITY. [*Received, September 4th*, 1918.]

LXXVI.—*Studies in the Phenylsuccinic Acid Series. Part VII. The Action of Alcohols and Amines on* r-*Diphenylsuccinic Anhydride.*

By HENRY WREN and HOWELL WILLIAMS.

THE present investigation was undertaken with the primary object of ascertaining whether derivatives of *meso*diphenylsuccinic acid are produced during the reaction of alcohols and amines with *r*-diphenylsuccinic anhydride. It has been pointed out previously by Anschütz and Bendix (*Annalen*, 1890, **259**, 73) that the *r*-anhydride is converted by hot water into a mixture of the *r*-acid (about 96 per cent.) and *meso*-acid (about 4 per cent.), and this result is corroborated by the observation of Wren and Still (T., 1915, **107**, 1451) that the optically active anhydrides, when treated

with hot water, pass into diphenylsuccinic acids of the same sign containing about 8 per cent. of optically inactive material, from which *meso*diphenylsuccinic acid can be isolated in very small quantity. The action of cold ethyl alcohol on the *l*-anhydride gave a rather more complex result. About 20 per cent. of inactive material appeared to be present in the crude product, from which however, a homogeneous substance could not be isolated; after crystallisation from light petroleum, a small quantity of substance was obtained which was not completely molten below 146°. Since ethyl hydrogen *l*-diphenylsuccinate melts at 113·5—114·5°, whilst Franchimont (*Ber.*, 1872, **5**, 1050) gave 140° as the melting point of the corresponding *r*-ester, it seemed valid to conclude that ethyl hydrogen *meso*diphenylsuccinate was also present. A not dissimilar result is recorded by Anschütz and Bendix (*loc. cit.*), who, by shaking *r*-diphenylsuccinic anhydride with chloroform containing ethyl alcohol, obtained a product analyses of which gave results in agreement with those required for the ethyl hydrogen ester, but the physical constants (melting point of crop, 164—168°; melting point of substance from mother liquor, 156—174°) appeared to show that the material was not uniform.

The experiments just quoted pointed thus to a very profound influence of the reagent on the mode of opening of the anhydride ring, but their significance was greatly discounted by the incidental observation that ethyl hydrogen *r*-diphenylsuccinate melts at 170—171° instead of at 140°, as recorded by Franchimont. The action of *r*-diphenylsuccinic anhydride on methyl and ethyl alcohols, on aniline, and on *p*-toluidine has therefore been studied, with the result that in the case of ethyl alcohol only has any definite evidence of the formation of *meso*-derivatives been obtained, and even in this instance the amount is very small.

The interaction of *r*-diphenylsuccinic anhydride and aniline has been studied by Anschütz and Bendix (*Annalen*, 1890, **259**, 92), who prepared diphenylsuccinanil by heating the anhydride with half its weight of aniline at 170—175°; on treatment with a boiling aqueous solution of barium hydroxide, the anil was converted into a diphenylsuccinanilic acid which melted at 220°. By the action of the anhydride on aniline dissolved in benzene, they isolated a substance which melted at 65—68°, resolidified at 105—108°, and again melted at 220°. A repetition of the latter experiment has led to a somewhat different result, since we find the crude product to melt at 173—176°, to resolidify at about 187°, and to melt again at 226°, the initial melting point, however, being somewhat dependent on the conditions of the determination; after purification, it yields a diphenylsuccinanilic acid

which melts at 173—175° with the evolution of gas, then resolidifies, and again melts at 227°. This appears to be practically the sole product of the change. It is readily transformed into diphenylsuccinanil either by the action of heat or by ethyl-alcoholic hydrogen chloride. Considering the conditions of their formation, it appears not unreasonable to regard the product melting at 173—175° as derived from the *r*-acid and that melting at 220° as belonging to the *meso*-series.

r-Diphenylsuccinic anhydride reacts very readily with a solution of *p*-toluidine in benzene, giving an almost quantitative precipitate of an acid melting at 195—196°, which appears to be the sole product of the action. This acid yields a barium salt which is sparingly soluble in water; it is readily transformed by the action of heat or of alcoholic hydrogen chloride into diphenylsuccino-*p*-tolil. The latter substance is converted by alkali into a mixture of acids which can be separated by taking advantage of the widely differing solubilities of their barium salts in water; from the less readily soluble portion, the acid melting at 195—196° can easily be isolated, whilst the more readily soluble portion yields an isomeric acid melting and decomposing at 206°, which is easily converted into diphenylsuccino-*p*-tolil. From the mode of formation, the relatively lower melting point and sparing solubility of the barium salt, it appears reasonable to conclude that the former acid belongs to the racemic series, the latter being therefore a derivative of the *meso*-type.

Experimental.

Partial Esterification of r- *and* meso-*Diphenylsuccinic Acids.*

Ethyl hydrogen *meso*diphenylsuccinate was obtained from the products of the incomplete esterification of the *meso*-acid by ethyl alcohol and sulphuric acid according to the Fischer-Speier method. Isolation was readily effected by shaking the crude product, obtained after removal of excess of alcohol, with water and chloroform, whereby unchanged *meso*-acid remained undissolved. The chloroform solution was agitated with concentrated sodium carbonate solution; the latter, when acidified, yielded an immediate precipitate of ethyl hydrogen *meso*diphenylsuccinate, which was purified by crystallisation from slightly aqueous alcohol and subsequently from benzene.

Ethyl hydrogen meso*diphenylsuccinate* separates from benzene in minute, colourless needles. It is readily soluble in cold chloroform or ether or in hot ethyl alcohol, and moderately so in cold ethyl alcohol. When heated, it shrinks to a thin core and melts

sharply at 174·5—175°. After being dried in a vacuum over calcium chloride, the ester retains half a molecule of water:

0·1461 gave 0·3765 CO_2 and 0·0816 H_2O. C = 70·3; H = 6·3.

0·5431 lost 0·0149 at 100—105°. H_2O = 2·74.

0·1393 * gave 0·3700 CO_2 and 0·0756 H_2O. C = 72·4; H = 6·1.

0·3885 neutralised 12·9 c.c. of 0·1033 *N*-sodium hydroxide. Calc.: 12·64 c.c.

$C_{18}H_{18}O_4,\frac{1}{2}H_2O$ requires C = 70·3; H = 6·3; H_2O = 2·93 per cent.

$C_{18}H_{18}O_4$ requires C = 72·5; H = 6·1 per cent.

Ethyl hydrogen *r*-diphenylsuccinate was similarly obtained by the incomplete esterification of *r*-diphenylsuccinic acid, and was purified through the sparingly soluble sodium salt, and finally by cautious crystallisation of the acid ester from a small quantity of ethyl alcohol. It may be more readily crystallised from aqueous alcohol or from a mixture of benzene and light petroleum (b. p. 80—100°), but the removal of small quantities of admixed *r*-acid is not easily accomplished in this manner.

Ethyl hydrogen r-*diphenylsuccinate* separates from alcohol in aggregates of ill-defined needles; it is readily soluble in the boiling, fairly readily so in the cold solvent. It dissolves readily in cold ether, fairly readily in cold benzene, sparingly in light petroleum. It melts at 170—171°:

0·4137 neutralised 13·9 c.c. of *N*/10-potassium hydroxide. Calc.: 13·88 c.c.

0·1725 gave 0·4575 CO_2 and 0·0944 H_2O. C = 72·3; H = 6·1.

$C_{18}H_{18}O_4$ requires C = 72·5; H = 6·1 per cent.

On complete esterification with ethyl alcohol and sulphuric acid, the acid ester was converted into ethyl *r*-diphenylsuccinate melting at 84·5—85·5°, thus confirming the position of the ester in the racemic series.

Sodium ethyl r-*diphenylsuccinate* separates from water, in which it is sparingly soluble at the ordinary temperature, in aggregates of fine needles:

0·2188 † lost 0·0395 at 100—110°. H_2O = 18·05.

$C_{18}H_{17}O_4Na,4H_2O$ requires H_2O = 18·37 per cent.

0·1788 ‡ gave 0·0386 Na_2SO_4. Na = 6·89.

$C_{18}H_{17}O_4Na$ requires Na = 7·20 per cent.

The salt evolved acrid fumes and became discoloured at 180°.

Barium ethyl r-*diphenylsuccinate* was prepared by neutralising a suspension of the ethyl hydrogen ester in water with barium hydroxide solution; it is moderately soluble in cold water:

* Dried at 100–105° until constant in weight.

† Air-dried. ‡ Dried at 100–110°.

0·3754 * lost 0·0177 at 100—110°. $H_2O = 4·72$.
$C_{36}H_{34}O_8Ba,2H_2O$ requires $H_2O = 4·70$ per cent.
0·2034 † gave 0·0662 $BaSO_4$. Ba = 19·12.
$C_{36}H_{34}O_8Ba$ requires Ba = 18·78 per cent.

Action of Ethyl Alcohol on r-*Diphenylsuccinic Anhydride.*

r-Diphenylsuccinic anhydride (8·1 grams) was allowed to remain in a stoppered flask, with occasional shaking, with ethyl alcohol (100 c.c.) until solution was complete, for which about three days were required. (A small portion of the solution was evaporated to dryness, and the residue was titrated with standard sodium hydroxide solution; the results indicated that the ethyl hydrogen ester contained a very small proportion of the free acid. This experience was confirmed in a number of other instances, and it therefore appears to be a matter of very considerable difficulty to prepare the alcohol absolutely free from moisture and to maintain it in this condition during the experiment.) The alcoholic solution was concentrated and exactly neutralised with aqueous-alcoholic sodium hydroxide solution. After complete removal of the alcohol, the aqueous solution was cooled, when sodium ethyl *r*-diphenylsuccinate was readily deposited (crop *A*). The precipitate was removed, and a second small crop of crystals was obtained by concentrating the filtrate. The mother liquor from the latter crop was acidified with hydrochloric acid and extracted with ether. The ethereal extract, after evaporation, left a small residue which melted indefinitely at 148—200°. It was completely esterified with ethyl alcohol and sulphuric acid; the mixture of normal esters was crystallised from ethyl alcohol, when ethyl *meso*diphenylsuccinate (about 0·4 gram) was obtained in well-defined needles which melted at 140—141°.

The crop *A* (see above) was decomposed with dilute hydrochloric acid; the precipitated acid ester (6·8 grams) melted sharply at 170—171°, and was in all respects identical with ethyl hydrogen *r*-diphenylsuccinate obtained by partial esterification of the *r*-acid.

Action of Methyl Alcohol on r-*Diphenylsuccinic Anhydride.*

r-Diphenylsuccinic anhydride (5 grams) was warmed with absolute methyl alcohol (40 c.c.) at 40° during six hours. The mixture was cooled and the precipitated acid ester removed; it melted at 196—198°, and proved to be pure methyl hydrogen *r*-diphenylsuccinate. The material obtained by evaporation of the filtrate melted at 194—198°; the esterification of the latter was completed

* Air-dried. † Dried at 100–110°.

as usual, but the only substance which could thus be isolated was methyl *r*-diphenylsuccinate.

Methyl hydrogen r-*diphenylsuccinate* separates from hot methyl alcohol, in which it is sparingly soluble, in small pyramids. It dissolves sparingly in boiling benzene, moderately readily in cold ether. It melts at 196—198° after slight previous sintering:

0·3303 neutralised 17·45 c.c. of 0·0666 *N*-alkali. Calc.: 17.47 c.c.
0·1847 gave 0·4878 CO_2 and 0·0948 H_2O. C=72·0; H=5·7.
$C_{17}H_{16}O_4$ requires C=71·8; H=5·7 per cent.

The *sodium* salt separates from its aqueous solution in small prisms:

0·4456 * lost 0·0962 at 100—110°. H_2O=21·6.
$C_{17}H_{15}O_4Na,4H_2O$ requires H_2O=19·05 per cent.
0·1690 † gave 0·0385 Na_2SO_4. Na=7·37.
$C_{17}H_{15}O_4Na$ requires Na=7·50 per cent.

Action of Aniline on r-*Diphenylsuccinic Anhydride.*

A solution of the *r*-anhydride (5 grams) in benzene (10 c.c.) was added to aniline (1·85 grams) dissolved in the same solvent (15 c.c.); in the course of a few seconds, a copious, white precipitate commenced to separate, and the solution speedily became semi-solid. The *r*-diphenylsuccinanilic acid, which was almost quantitatively precipitated, melted at 168—169°, resolidified, and again melted at 226·5—229°. It was crystallised from a small quantity of warm alcohol.

r-*Diphenylsuccinanilic acid* separates from alcohol in short prisms. It is readily soluble in warm alcohol or benzene, in cold ether or acetone, less readily so in carbon tetrachloride or light petroleum. It dissolves sparingly in cold alcohol or benzene. It melts and evolves gas at 173—175°, resolidifies at a slightly higher temperature, and again melts at 227°; the observed values depend somewhat on the rate of heating and the diameter of the tubes used:

0·1853 gave 0·5163 CO_2 and 0·0939 H_2O. C=76·0; H=5·7.
0·3721 „ 13·6 c.c. N_2 at 16° and 765 mm. N=4·3.
$C_{22}H_{19}O_3N$ requires C=76·5; H=5·5; N=4·1 per cent.

Conversion of r-*Diphenylsuccinanilic Acid into Diphenylsuccinanil.*

A. *By the Action of Heat.*—*r*-Diphenylsuccinanilic acid was gradually heated to 230°, when complete fusion was obtained. The substance solidified, when cooled, to a pale yellow mass which,

* Air-dried. † Dried at 100–110°.

after being crystallised from benzene, yielded fine, colourless needles; these were identified as diphenylsuccinanil from the melting point (229—230° after slight shrinkage at 227°) and analysis (Found: C=80·9; H=5·2. Calc.: C=80·7; H=5·2 per cent.). Anschütz and Bendix (*loc. cit.*) describe the substance as separating from benzene in fine, colourless needles which melt at 226—227°, from acetic acid in larger, shining needles melting at 230—231°.

B. *By the Action of Ethyl-alcoholic Hydrogen Chloride.*—The acid (1·1 grams) was gently warmed with a 3 per cent. solution of hydrogen chloride in ethyl alcohol; it did not immediately dissolve, but, on reaching the boiling point, a copious, crystalline precipitate speedily separated. Boiling was continued during four hours, during which no change in the appearance of the product was observed. The alcohol was removed, and the residue crystallised from benzene, when diphenylsuccinanil (0·7 gram) melting at 229—230° was readily obtained.

The behaviour of *r*-diphenylsuccinanilic acid under these conditions is thus similar to that of the anilic acid, melting at 220°, described by Anschütz and Bendix.

Action of p-*Toluidine on* r-*Diphenylsuccinic Anhydride.*

Molecular quantities of *r*-diphenylsuccinic anhydride and of *p*-toluidine were dissolved in benzene and mixed; after a few seconds, the solution became cloudy, and in the course of a few minutes, *r*-diphenylsuccino-*p*-toluidic acid was almost quantitatively precipitated. The crude substance melted and evolved gas at 194—196°. It was crystallised from slightly aqueous alcohol.

r-*Diphenylsuccino*-p-*toluidic acid* separates from aqueous alcohol in small needles. It is readily soluble in hot alcohol, sparingly so in hot benzene, and very sparingly so in hot water; it dissolves readily in cold acetone or ether, less readily in cold chloroform. It melts at 195—196° and does not appear to suffer decomposition below 270°:

0·1613 neutralised 6·8 c.c. of 0·0666 *N*-alkali. Calc.: 6·75 c.c.
0·1850 gave 0·5229 CO_2 and 0·0960 H_2O. C=77·1; H=5·8.
0·3842 ,, 12·8 c.c. N_2 at 18° and 762 mm. N=3·95.
$C_{23}H_{21}O_3N$ requires C=76·9; H=5·9; N=3·90 per cent.

At its melting point, *r*-diphenylsuccino-*p*-toluidic acid loses water and passes into the tolil (see later). With slightly impure specimens of the acid, this decomposition is very evident, and water vapour is freely evolved. With the pure acid, however, some external impulse appears requisite to render this effect manifest.

Silver r-*diphenylsuccino*-p-*toluidate* forms a voluminous, white powder:

0·3275 gave 0·0744 Ag. Ag = 22·72.

$C_{23}H_{20}O_3NAg$ requires Ag = 23·16 per cent.

Methyl r-*diphenylsuccino*-p-*toluidate* was prepared by the action of an excess of methyl iodide on dry silver diphenylsuccino-*p*-toluidate, and was purified by crystallisation from a small quantity of ethyl alcohol, from which it separates in well-defined, microscopic needles melting at 173—174·5°:

0·1395 gave 0·3923 CO_2 and 0·0807 H_2O. C = 76·7; H = 6·5.

$C_{24}H_{23}O_3N$ requires C = 77·2; H = 6·2 per cent.

Conversion of r-*Diphenylsuccino*-p-*toluidic Acid into Diphenylsuccino*-p-*tolil.*

A. *By the Action of Ethyl-alcoholic Hydrogen Chloride.*—The acid (1·8 grams) was heated under reflux with ethyl-alcoholic hydrogen chloride solution (8 per cent.; 10 c.c.). A homogeneous solution was readily obtained, from which a precipitate separated after a few minutes. The solvent was removed on the water-bath and the residue purified by crystallisation from much alcohol.

Diphenylsuccino-p-*tolil* separates from boiling ethyl alcohol in long, slender needles which, although apparently perfectly stable when dry, frequently crumble to microscopic prisms when preserved beneath the mother liquor. It dissolves sparingly in the boiling, very sparingly in the cold solvent; it is readily soluble in cold acetone, moderately so in cold chloroform or benzene, and sparingly so in cold ether. It melts at 170°:

0·1739 gave 0·5182 CO_2 and 0·0884 H_2O. C = 81·3; H = 5·7.

$C_{23}H_{19}O_2N$ requires C = 80·9; H = 5·6 per cent.

B. *By the Action of Heat.*—The *r*-acid was heated in a small tube at 195—205° during fifteen minutes, at the end of which period the evolution of gas had ceased. The residue was crystallised from alcohol, from which it separated in slender needles which disintegrated to microscopic prisms. It melted at 170°, and was thus identified as diphenylsuccino-*p*-tolil.

The behaviour of *r*-diphenylsuccino-*p*-toluidic acid is thus very similar to that of the corresponding anilic acid; it is, however, curious that the melting point of the tolil is lower than that of the toluidic acid, whilst the reverse is the case with the aniline derivatives.

Action of Alkali on Diphenylsuccino-p-tolil.

Diphenylsuccino-*p*-tolil (5 grams) was boiled during forty-five minutes with aqueous-alcoholic sodium hydroxide solution (1·2*N*; 40 c.c. Water : alcohol : : 1 : 3). The sodium salts thus formed were converted into the barium derivatives, which were separated by treatment with water. From the less readily soluble salt, *r*-diphenylsuccino-*p*-toluidic acid, melting at 194—195°, was easily isolated; the more readily soluble portion yielded, on acidification, crude *meso*diphenylsuccino-*p*-toluidic acid, which was purified by crystallisation from slightly diluted acetic acid.

meso*Diphenylsuccino*-p-*toluidic acid* separates from alcohol or dilute acetic acid in minute, colourless needles which melt and decompose slightly at 206°. It is moderately soluble in cold methyl or ethyl alcohol or in acetic acid, sparingly so in water or hot benzene, readily so in ether or acetone, and practically insoluble in light petroleum or carbon tetrachloride. When heated at 215° during five minutes or boiled with ethyl-alcoholic hydrogen chloride, it is transformed into diphenylsuccino-*p*-tolil:

0·1216 neutralised 3·4 c.c. of *N*/10-sodium hydroxide. Calc.: 3·39 c.c.

0·1457 gave 0·4128 CO_2 and 0·0804 H_2O. C = 77·25; H = 6·13. $C_{23}H_{21}O_3N$ requires C = 76·88; H = 5·85 per cent.

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LXXVII.—*The Inflammation of Mixtures of Methane and Air in a Closed Vessel.*

By RICHARD VERNON WHEELER.

WHEN an inflammable mixture of gas and air is ignited within an inflexible closed space, flame travels throughout the mixture in a manner and at a speed dependent mainly on the nature and proportion of the inflammable gas present. The manner in which the flame spreads through the mixture is affected also by the shape

of the containing vessel and the position of the point of ignition, and the speed of the flame is affected by these factors as well as by the intensity of the means of ignition and the initial temperature and pressure of the mixture. To such causes of variation in the manner and speed of the spreading of flame must be added mechanical agitation or turbulence of the mixture, such as is induced, for example, within a gas-engine cylinder during the introduction of the charge (see Dugald Clerk, "The working fluid of internal-combustion engines," Gustave Ganet Lecture, Junior Institution of Engineers, 1913).

The inflammation of the mixture within the closed vessel, inasmuch as it results in the formation of products of combustion at a high temperature, causes an increase of pressure. If the vessel were impervious to heat, the maximum pressure developed would afford a measure of the thermal energy of the products of combustion, which should be equal to the chemical energy of the uninflamed mixture.

The present paper records the results of a study of the inflammation of different mixtures of pure methane and air in closed spherical vessels. The principal data obtained were: (1) the maximum pressures developed, (2) the rates of development of pressure, and (3) the speeds of propagation of flame. Details as to the manner in which these data were obtained, and of the precautions taken to ensure their accuracy, are given in the experimental portion of the paper.

Development of Pressure.

In the table that follows are given the maximum pressures developed by different mixtures of methane and air when ignited within spherical vessels of about (*a*) 4 litres and (*b*) 16 litres capacity, 19·5 and 31·2 cm. in diameter, respectively. For comparison, Mallard and Le Chatelier's determinations (*Ann. des Mines*, 1883, [viii], **4**, 379), for which they used a cylindrical vessel 17 cm. long and 17 cm. in diameter, are included in the table on p. 842.

These results are shown graphically in Fig. 1. It is of importance to notice that the maximum pressures for similar mixtures in the 4-litre and the 16-litre spheres, as determined by interpolation, are practically identical.

The values quoted as Mallard and Le Chatelier's are their observed values (*loc. cit.*, p. 509). They are rather irregular and are considerably higher than the results obtained for similar mixtures in the spheres. This may be due to impurity of the com-

Methane in mixture. Per cent. by volume.	Maximum recorded pressures above atmospheric. Atmospheres. 4-Litre sphere.	16-Litre sphere.	3·86-Litre cylinder (Mallard and Le Chatelier).
6·05	—	2·86	—
6·30	3·20	—	—
6·80	5·10	—	5·51
6·85	—	4·35	—
7·45	5·64	—	—
7·80	—	5·85	—
7·95	6·09	—	—
8·00	—	—	6·53
8·45	6·40	—	—
8·80	—	6·66	—
9·20	6·73	—	7·41
9·40	6·80	—	—
9·50	—	—	7·75
9·65	6·90	—	—
9·80	—	6·94	7·55
10·00	—	—	7·34
10·10	6·97	—	—
10·25	6·97	—	—
10·60	—	—	7·48
10·75	6·87	—	—
10·80	—	6·80	—
11·20	—	—	6·94
11·40	6·73	—	—
11·90	—	6·40	—
12·10	6·36	—	—
12·50	—	—	6·46
12·80	—	5·78	—
12·90	5·78	—	—
13·40	4·80	—	—
13·90	3·54	—	—

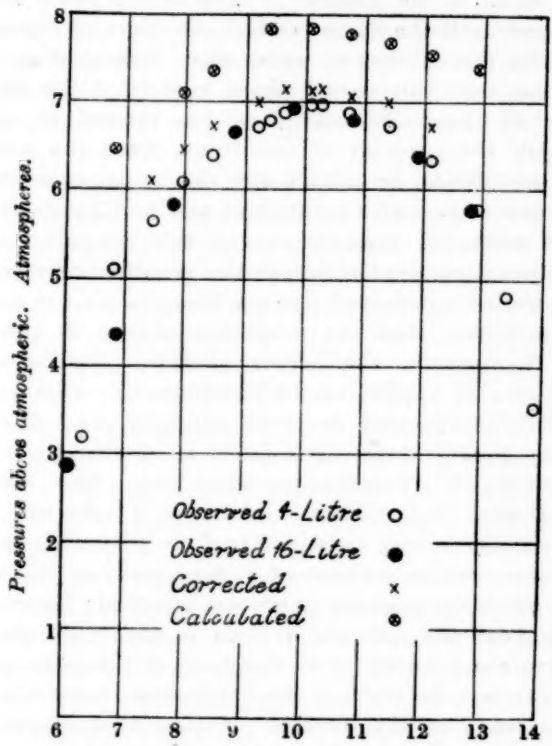
bustible gas used, regarding which the fact is recorded (*loc. cit.*, p. 409) that it contained some gas richer in carbon than methane. The gas was prepared from sodium acetate, and would contain ethylene and acetone vapour.

Reference should be made also to some experiments by Beyling (*Glückauf*, 1906, **42**, 130), who used a cylindrical vessel of 42 litres capacity, 33·5 cm. in diameter and 42·5 cm. long. The maximum pressure recorded as produced by any mixture of methane and air was 6·5 atmospheres. In a vessel of smaller capacity (about 11 litres) the maximum pressure was the same.

By reason of the shape of their explosion-vessel, Mallard and Le Chatelier found it necessary to introduce a correction for cooling during the propagation of flame, averaging about 10 per cent. on their observed pressures. If ignition of an inflammable mixture is exactly at the centre of a perfectly spherical vessel, it is probable that the propagation of flame follows regular concentric spherical surfaces in such a manner that the flame reaches the

walls of the vessel simultaneously at all points; for, except with very slowly moving flames, or, possibly, in very large vessels, it is unlikely that convection currents will have time materially to affect the speed in any particular direction. The whole of the mixture is thus inflamed before cooling by conduction of heat by the walls of the vessel can come into play.*

FIG 1.



If, however, the vessel is not perfectly spherical, or if ignition is not truly central, flame will touch the walls sooner at some places than at others, and cooling of the products of combustion will begin before propagation of flame is complete. The maximum

* Cooling by the walls, before the whole mixture is inflamed, may cause a negligible loss of heat if the unburnt mixture in contact with them is heated by compression (due to dilation of the burnt mixture at the centre of the vessel) before flame reaches it.

pressure within the vessel as recorded by a gauge is not then that which the mixture would exert were the whole brought at once to the temperature of combustion. The fact that Mallard and Le Chatelier used a cylinder for their experiments, although they ignited the mixture at the centre, caused the propagation of flame within the vessel to assume two phases. During the first phase the flame travelled from the centre as, presumably, a spherical envelope until it touched the walls of the vessel (the height of which was equal to the diameter). The second phase then began and continued until the flame reached the curve of intersection of the ends with the cylindrical walls, when inflammation was complete. Throughout this second phase, cooling of the products of combustion by the walls took place, the amount of cooling increasing with the progress of the flame, since the area of the surface of the cylinder in contact with the heated gases increased.

A correction to be added to Mallard and Le Chatelier's recorded figures for maximum pressures is, on this reasoning, necessary. The correction when applied brings the pressures developed by all their mixtures of "methane" and air from one to one and a third atmospheres higher than the pressures recorded in the spherical vessels. The question then arises whether a similar correction should not also be applied to the latter results—whether, in fact, one is justified in assuming that with central ignition in a spherical vessel flame spreads at the same speed in all directions. Langen ("Mitteillungen u. Forschungsarbeiten aus dem Gebeite des Ingenieurwesens," vol. 8, 1903), who used a spherical vessel for similar experiments, did, indeed, introduce a "cooling correction." This, however, was on account of a short neck, at the top of the sphere, to which the pressure-gauge was attached; Langen assumed that throughout the spherical portion of his vessel the flame in any given mixture spread in all directions at the same speed.

In order to test the truth of this supposition, a series of measurements was made of the intervals of time that elapsed between ignition and the advent of flame at the top and bottom of a closed vessel filled with different mixtures of methane and air. With all mixtures containing more than 7·5 and less than 12·5 per cent. of methane, the time-intervals for upward and for downward propagation of flame were identical. They coincided also for each mixture with the time that elapsed between ignition and the attainment of maximum pressure in a vessel of the same dimensions. With mixtures containing less than 7·5 and more than 12·5 per cent. of methane, in which the rate of propagation of flame is slow, flame reached the bottom of the vessel later than it reached the top by an amount of time which varied with the methane-con-

tent of the mixture. Thus the measurements for three mixtures were:

Methane in mixture. Per cent.	Time required for the flame to travel 9·75 cm. from the point of ignition. Upwards.	Downwards.
6·40	0·260 sec.	0·468 sec.
6·95	0·169 ,,	0·234 ,,
13·00	0·219 ,,	0·320 ,,

With such mixtures, therefore, cooling of the products of combustion takes place before the attainment of the maximum recorded pressure, even in a spherical vessel, by reason of the contact of the upper part of the flame with the walls of the vessel before the lower part of the mixture is burnt.

It should be noted that the limits of inflammability of methane–air mixtures ignited at the centre of a closed spherical vessel are 5·6 per cent. lower and 14·8 per cent. upper (T., 1911, **99**, 2013). The progress of the flame in these mixtures is sufficiently slow to follow by the eye; the flame travels upwards from the spark as an inverted cone, fills the upper third of the vessel, and thence travels slowly downwards as a horizontal disk to the bottom.

With the mixtures containing more than 7·5 and less than 12·5 per cent. of methane, however, no loss of heat through cooling by the walls before the whole of the mixture has been inflamed should arise in a spherical vessel, other than the negligible quantity transmitted by the layer in contact with the walls during the interval of time that elapses between its compression by the inflamed core (and consequent heating) and its burning. Over this range, then, no such correction for cooling as Mallard and Le Chatelier and Langen applied is required when perfectly spherical vessels are used and ignition is at the centre. One would arrive at the same conclusion from the fact, already noted, that the maximum pressures recorded were the same, within 1 per cent., over the range 7·5 to 12·5 per cent. of methane, in the 4-litre as in the 16-litre sphere, although the ratio surface/volume was 1·6 times as great with the former as with the latter.

Experiment thus shows that one is justified in assuming, over the major portion of the range of inflammable mixtures of methane and air, no loss of heat in a spherical vessel due to contact of part of the flame with the walls before the whole of the mixture is burnt. Yet one cannot assume that the maximum recorded pressure in such a vessel gives a measure of the internal energy of the products of combustion, which should be equal to the chemical energy of the uninflamed mixture, or, in other words,

that the pressure recorded is that which would be attained were the vessel impervious to heat.

Apart from loss by radiation during the propagation of flame, it must be remembered that at the moment when the vessel is just filled with flame (that is, at the moment of maximum recorded pressure in a spherical vessel), the products of combustion are not in thermal equilibrium (see, in this connexion, the First Report [1910] of the Committee, appointed by the British Association, for the investigation of gaseous explosions). Hopkinson, *Proc. Roy. Soc.*, 1906, [*A*], **77**, 387) has shown that at the moment of maximum pressure of a mixture of coal gas and air, the temperature around the point of ignition at the centre of a cylindrical vessel was several hundred degrees higher than the mean temperature (as deduced from the pressure), owing to adiabatic compression of the products of combustion there during the burning of the remainder of the mixture; whilst at the sides and ends of the vessel, where the gases were compressed before ignition, the temperature reached was as much below the mean.

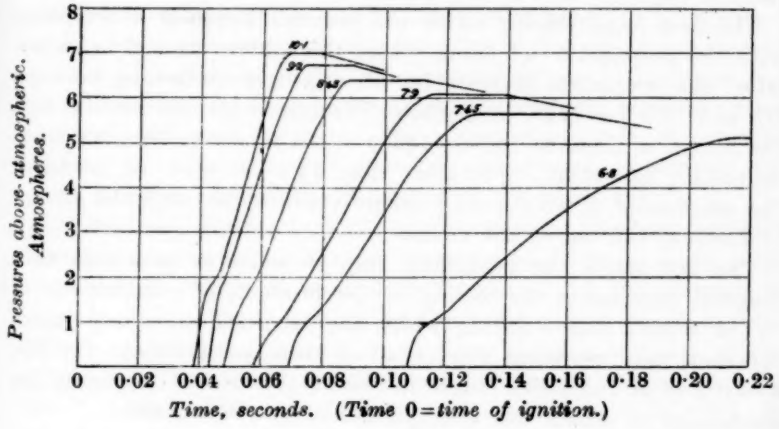
If the volumetric heats of the gases comprising the products of combustion were constant at all temperatures, the attainment of a uniform temperature within a closed vessel by convection and conduction would cause no alteration in pressure; but inasmuch as the volumetric heats are not constant, being perhaps half as great again in the hottest as in the coldest part of the gaseous mass, the attainment of thermal equilibrium should be attended by a change of pressure.

During the time that thermal equilibrium is being established, after complete inflammation has taken place, the cold walls of the spherical containing vessel are everywhere in contact with hot gases, so that simultaneously with any increase in pressure that might result from the equalisation of the temperature differences within the gaseous mass, there is a reduction of pressure due to loss of heat by conduction. This loss, and radiation losses during the same period as well as during the propagation of flame, combine to render the recorded pressures lower than those representative of the chemical energy of the uninflamed mixtures. It is difficult to make even a rough calculation of the change of pressure that should occur owing to the establishment of thermal equilibrium, because of lack of knowledge of the distribution of temperature within a spherical vessel at the moment of complete inflammation. It is possible, however, if certain assumptions are made, to obtain some idea of the order of magnitude of the pressure change from an examination of the time–pressure diagrams.

Diagrams for representative mixtures used in the 4-litre sphere

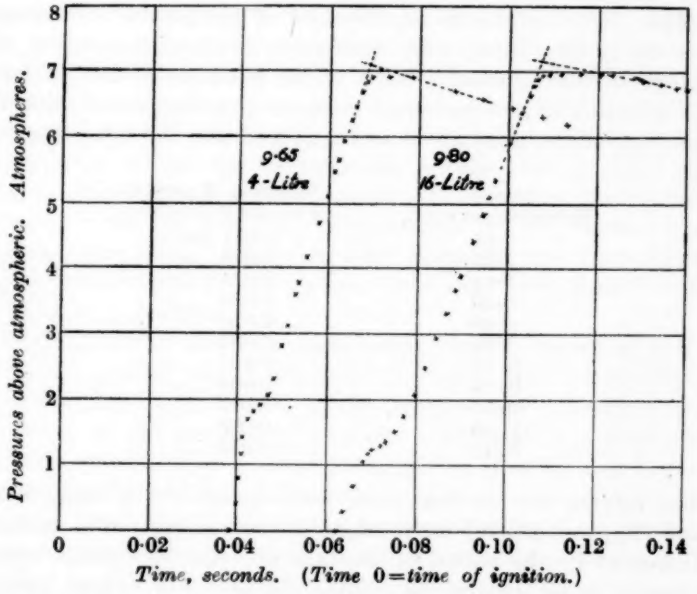
are shown in Fig. 2, whilst in Fig. 3 are given the diagrams for mixtures of nearly the same methane-content, the one (9·65 per

FIG. 2.



cent. methane) in the 4-litre and the other (9·80 per cent. methane) in the 16-litre sphere. These diagrams are reproduced on a

FIG. 3.



different scale from the actual records of the indicator in the manner described in the experimental portion of this paper.

Examination of these curves shows that each exhibits three stages of development. During the first stage the pressure increases proportionately with the time, during the second it remains constant, and during the third it gradually decreases.

The first stage, during which the pressure increases, corresponds with the propagation of flame within the sphere; as will be shown later, the maximum pressure for all mixtures containing between 7·5 and 12·5 per cent. of methane is attained simultaneously with the advent of flame at the boundary of the mixture. For mixtures containing less than 7·5 or more than 12·5 per cent. of methane, the attainment of maximum pressure synchronises with the advent of flame at the top of the vessel.

The last stage, the beginning only of which is shown in each diagram, represents the cooling of the products of combustion.

The second stage, during which the recorded pressure remains constant, may represent any or all of three possibilities: (1) The occurrence of successive stages in the combustion of methane, the mechanism of which can be represented by the equation

$$CH_4 + O_2 = (CH_2O + H_2O) = CO + H_2 + H_2O,$$

with subsequent burning of the carbon monoxide and hydrogen if oxygen is in excess; (2) exothermic secondary reaction between carbon monoxide and steam (compare Bone, *Phil. Trans.*, 1915, [*A*], **215**, 318); or (3) the equalisation of temperature differences within the gaseous mass, with consequent increase of pressure due to change in the volumetric heats of the products of combustion.

The duration of the period of constant pressure varies with the composition of the mixture of methane and air, the time intervals being:

Methane, per cent.	Duration of period of constant pressure.
7·45	0·031 sec.
7·95	0·026 ,,
8·45	0·024 ,,
9·20	0·016 ,,
9·40	0·010 ,,
9·65	0·009 ,,
10·10	0·010 ,,
10·25	0·009 ,,
10·75	0·013 ,,
11·40	0·018 ,,
12·10	0·024 ,,

These figures are not consistent with either of the suppositions (1) and (2) given above; for if stages in the combustion of methane are indicated by the period of constant pressure, one would expect that period to be shorter the greater the excess of oxygen present in the mixture, whilst the occurrence of the exothermic secondary reaction between carbon monoxide and steam should be most pro-

nounced when there is excess of methane above that required for complete combustion to carbon dioxide and steam.

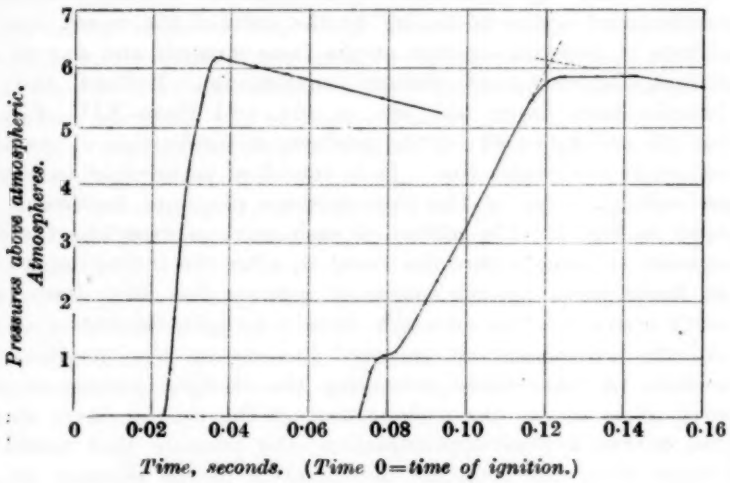
On the other hand, the figures support the view that the change of volumetric heats of the gases during the attainment of thermal equilibrium is responsible for an increase of pressure balancing a decrease due to cooling; for the duration of the period of constant pressure is shorter the higher the pressure attained, that is to say, the higher the mean temperature of the products of combustion. Moreover, reference to Fig. 3 shows that the period of constant pressure for mixtures of about the same methane-content was nearly twice as long in the 16-litre as in the 4-litre sphere.

Let us, then, assume that the second stage in the time–pressure diagrams represents a balance between a gradual decrease of pressure that begins as soon as inflammation of the mixture is complete and is due to cooling by the walls of the vessel, and an increase of pressure incident at the same moment and due to the gradual attainment of thermal equilibrium. Mallard and Le Chatelier have shown (*loc. cit.*, p. 454, and Plate XIV, Fig. 8) that the cooling curve for the products of combustion of methane and air is a straight line. It is therefore permissible to extend the cooling curves of the time–pressure diagrams backwards, as shown in Fig. 3. The portion of each curve representing the propagation of flame within the vessel is, after the initial impetus to the flame given by the source of ignition has died down, also nearly a straight line, although there is a slight diminution in the rate of development of pressure just before the maximum is reached. A line drawn extending the straight portion of this curve so as to cut the prolongation of the cooling curve should give, within a close approximation, the pressure that would be attained after the complete inflammation of the mixture did no cooling take place. This has been done for the two curves in Fig. 3, from which it will be seen that the "correction" amounts to, at most, 3 per cent.

The validity of the assumption that such a correction can and should be applied might be tested if means could be employed to ensure a rapid equalisation of the temperature differences within the vessel at the moment of complete inflammation. Experiments made in the course of another investigation (see "Third Report of the Explosions in Mines Committee," p. 26, London, 1913), during which a small fan was rapidly revolved within the sphere, may serve to illustrate the effect of aiding convection currents. The fan had four helical blades and was run at the rate of 100 revolutions per second. The results of a pair of experiments, one with and the other without the fan, using a mixture of ethane and air

containing 4·05 per cent. of ethane, are shown in Fig. 4. The maximum pressure recorded when the fan was revolving was higher than when the mixture was at rest by 0·23 atmosphere, an amount a little more (0·07 atmosphere) than the "correction" obtained in the manner described. This diagram illustrates also the effect of turbulence of the mixture on the speed of inflammation, an effect already noted by Dugald Clerk and Hopkinson. With the fan running, the time taken, measured from the moment of ignition, for the attainment of maximum pressure was 0·0362 sec.; without the fan, it was 0·1244 sec. No doubt the higher pressure reached in the former experiment was in part due to smaller radiation loss during the more rapid propagation of flame.

FIG. 4.



Whatever the cause of evolution of heat, the horizontal portion of the time–pressure diagram represents a balance between heat evolved after flame has travelled throughout the mixture and heat dissipated, and the correction to be applied on this score cannot exceed the quantity deduced by extrapolation of the cooling and propagation curves. In Fig. 1 are shown the "corrected" pressures for mixtures over the range 7·5 to 12·5 per cent. of methane, together with the calculated maximum pressures those mixtures should produce, taking Langen's values for the specific heats of the various gases and assuming no loss of heat by radiation.

The calculated values are about 10 per cent. greater than the observed over the whole range. This difference, assuming the

correctness of the values taken for the specific heats of the gases, must be due mainly to loss of heat by radiation during the propagation of flame in the spheres, for it has been shown that up to the time of attainment of maximum pressure flame does not touch the walls of the vessels.* For information regarding the probable loss of heat by radiation, only the results of Hopkinson (*Proc. Roy. Soc.*, 1911, [*A*], **84**, 155) with mixtures of coal-gas and air, and of David (*Phil. Trans.*, 1912, [*A*], **211**, 375) with coal-gas–air and hydrogen–air mixtures are available, and direct comparison of these with methane–air mixtures cannot be made.

It has been shown, however (David), that up to the time of maximum pressure (attained in 0·05 sec.), a 15 per cent. coal-gas–air mixture radiated about 3 per cent. of its total heat of combustion, the maximum temperature reached being 2400° abs. A 25·4 per cent. hydrogen–air mixture, which developed the same maximum temperature, radiated about 0·5 per cent. only of its total heat of combustion up to the time of attainment of maximum pressure (in 0·017 sec.). The coal-gas used probably contained about 50 per cent. of hydrogen and 35 per cent. of methane (and other hydrocarbons); it is known that the radiation from the mixtures is due almost entirely to the steam and carbon dioxide that they contain, and that carbon dioxide has a radiating power about 2·4 times that of an equal volume of steam (R. von Helmholtz, "Die Licht- und Warmestrahlungverbrennender Gase," Berlin, 1890); an estimated loss due to radiation of about 10 per cent. of the total heat of combustion during the propagation of flame in the mixtures of methane and air may therefore be not far from the truth.

Propagation of Flame.

Each of the time–pressure diagrams shown in Figs. 2 to 4 has been plotted with the time of passage of the secondary discharge that caused the ignition of the mixture as zero time. It has been assumed by the majority of experimenters on the inflammation of gaseous mixtures in closed vessels that the time of ignition synchronises with the time of first manifestation of pressure on the indicator or gauge. Bairstow and Alexander (*Proc. Roy. Soc.*, 1905, [*A*], **76**, 340) found, however, that this was not so in their experiments with mixtures of coal-gas and air; and it is apparent from the diagrams for methane–air mixtures given in this paper that there is a definite interval of time, the length of which depends on the composition of the mixture, between the ignition

* A slight amount of cooling no doubt arises through conduction of heat by the electrodes.

of the mixture at the centre of a spherical vessel and the first appearance of pressure on an indicator fixed at the top.

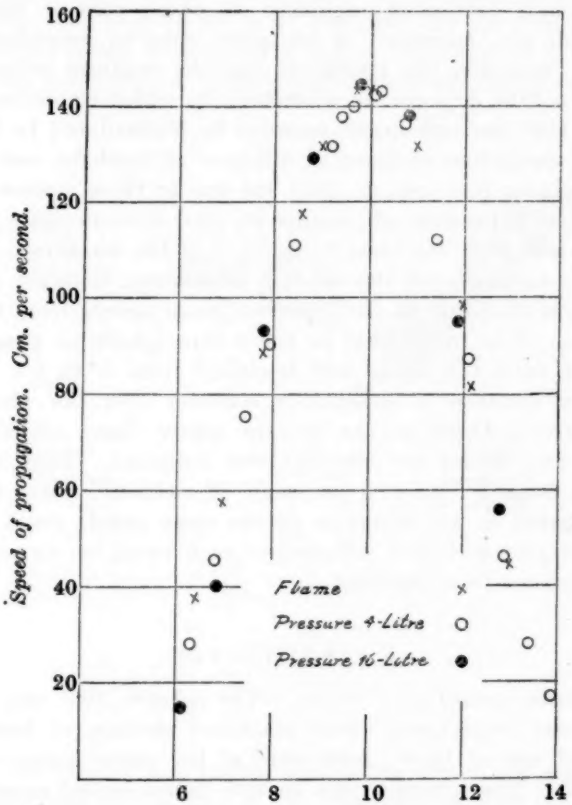
In order to be able to trace the progress of the flame within the vessels from the time–pressure diagrams, records were taken of the time that elapsed between the passage of an electric spark at the centre of a closed vessel containing different mixtures of methane and air and the appearance of flame at a point 7·5 cm. vertically upwards, in the manner described in the experimental portion of this paper. The time-intervals calculated for a distance of 9·75 cm. were found to correspond closely with the times taken for the development of the maximum pressures in similar mixtures in the 4-litre sphere (radius, 9·75 cm.), as the following table

		4-Litre sphere.		16-Litre sphere.		
Methane in mixture. Per cent.	Time taken for flame to travel 9·75 cm. upwards. Seconds.	Time between ignition and first appearance of pressure. Seconds.	Time between ignition and attainment of maximum pressure. Seconds.	Time between ignition and first appearance of pressure. Seconds.	Time between ignition and attainment of maximum pressure. Seconds.	Mean speed of flame. Cm. per sec.
6·05	—	—	—	0·4233	1·0370	15
6·30	—	0·1800	0·3484	—	—	28
6·40	0·260	—	—	—	—	37·5
6·80	—	0·1080	0·2150	—	—	45·5
6·85	—	—	—	0·1830	0·3877	40
6·95	0·169	—	—	—	—	58
7·45	—	0·0690	0·1302	—	—	75
7·80	0·110	—	—	0·1021	0·1680	89, 93
7·95	—	0·0574	0·1084	—	—	90
8·45	—	0·0484	0·0878	—	—	111
8·60	0·083	—	—	—	—	117·5
8·80	—	—	—	0·0713	0·1206	129
9·00	0·074	—	—	—	—	132
9·20	—	0·0428	0·0720	—	—	132
9·40	—	0·0392	0·0707	—	—	138
9·65	—	0·0382	0·0696	—	—	140
9·70	0·068	—	—	—	—	143·5
9·80	—	—	—	0·0623	0·1080	144·5
10·00	0·068	—	—	—	—	143·5
10·10	—	0·0383	0·0684	—	—	142·5
10·25	—	0·0382	0·0682	—	—	143
10·75	—	0·0395	0·0715	—	—	136
10·80	—	—	—	0·0665	0·1130	138
11·00	0·074	—	—	—	—	132
11·40	—	0·0498	0·0870	—	—	112
11·90	—	—	—	0·1000	0·1640	95
12·00	0·099	—	—	—	—	98·5
12·10	—	0·0694	0·1164	—	—	87
12·20	0·120	—	—	—	—	81
12·80	—	—	—	0·1320	0·2800	56
12·90	—	0·1150	0·2120	—	—	46
13·00	0·219	—	—	—	—	44·5
13·40	—	0·1600	0·3470	—	—	28
13·90	—	0·2150	0·5700	—	—	17

shows. In the same table are given the time-intervals between ignition and the attainment of maximum pressure in the 16-litre sphere (radius, 15·6 cm.) and the calculated mean speeds of the flames in cm. per second.

The correspondence between the time taken for flame to travel from the centre to the top in the spheres and the time taken for

FIG. 5.



the attainment of the maximum pressures is perhaps best shown in Fig. 5, where the mean speeds of the flames, in cm. per sec., are plotted against percentages of methane in the mixtures, different symbols being used according as the points on the curve are (1) actual determinations of the rate of travel of flame, (2) calculated from the time-interval between ignition and the attainment of maximum pressure in the 4-litre sphere, or (3) calcu-

lated from the time-interval between ignition and the attainment of maximum pressure in the 16-litre sphere.

It is of interest to compare these speeds with the speeds during the "uniform movement" of flame in similar mixtures (see T., 1917, **111**, 1044), although the conditions under which propagation takes place are different. The shapes of the speed–percentage curves for the two modes of propagation are similar, the speeds in each exhibiting maxima over the range 9·5 to 10·5 per cent. methane and decreasing regularly on either side of this range. The speeds are, moreover, of the same order of magnitude (compare, for example, the speeds during the uniform movement of flame in a tube 30·5 cm. in diameter), in which connexion it may be noted that the high speeds recorded by Mallard and Le Chatelier for the propagation of flame in mixtures of methane and air in a closed cylinder (*loc. cit.*, p. 464) are due to those authors regarding the first indications of pressure on their time–pressure diagrams as coincident with the times of ignition of the mixtures.

If it is assumed, for the sake of calculation, that the flames in the spheres travelled at the observed mean speeds from the point of ignition, it is found that in the 4-litre sphere no pressure was indicated until the flame had travelled from 5 to 5·5 cm. (the calculated distance is remarkably constant over the whole range of mixtures), whilst in the 16-litre sphere flame travelled from 9 to 10 cm. before any pressure was indicated. That is to say, over the range 7·5 to 12·5 per cent. of methane, where the flame is propagated in all directions at the same speed, about one-fifth of the mixture had been inflamed in each vessel before any indication of pressure was obtained.

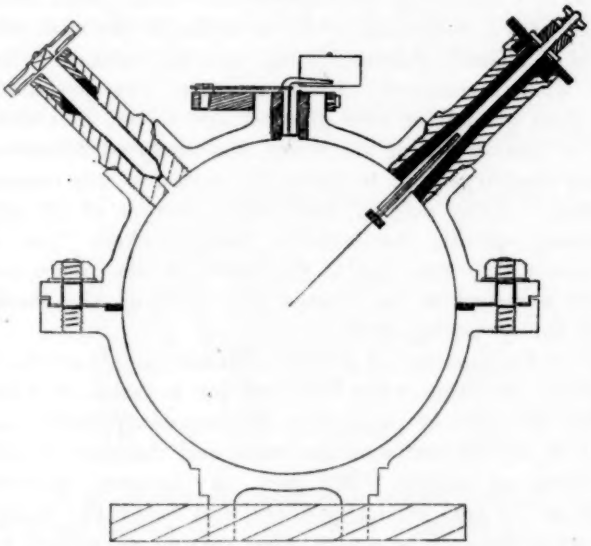
Experimental.

The Measurement of Pressure.—The spheres, 19·5 and 31·2 cm. in diameter respectively, were machined castings of bronze. A section of one of them—both were of the same design—is shown in Fig. 6. The sphere is cast in two halves bolted together with a loose ring of copper as washer. It is pierced at the top by a hole carrying a fixed sleeve of hardened steel, highly polished, the internal diameter of which is 12·75 mm. A hollow piston of hardened steel is ground and polished to fit the sleeve; the surface of the piston on which the pressure within the vessel acts is 78·5 sq. mm., the piston being prevented from passing through the sleeve by a thin ring of steel at the base thereof. Other fittings are: (*a*) a valve for exhaustion and the introduction of the inflammable mixture, (*b*) insulated electrodes reaching to the centre,

(*c*) a small window of quartz, and (*d*) a removable shaft carrying a small broad-bladed fan. The last-named was removed during all the experiments described in this paper, save the one wherein the use of the fan is specified. The fittings on the sphere for the piston, valve, and quartz window are flush with the inner surface, which is highly polished. Both spheres were made by Mr. C. W. Cook, of the University Engineering Works, Manchester.

The manometer is a triangular plate of tempered steel 2·6 mm. in thickness, the base of which is clamped, the apex making contact with the hollow piston in the sphere by means of a loose rod of steel, the lower end of which rests in a conical depression at the

FIG. 6.



centre of the base of the piston, whilst the upper end rests in a similar depression in the spring. A thin strip of steel is attached to the apex of the spring and carries a scribing style, which rests lightly against the surface of a smoked paper band on a drum revolved by an electric motor.

With this form of spring, the maximum strain is the same at all cross-sections, and the inertia is small, since it is the narrow part of the spring which moves most and the wide part least. The deflexion of the scribing style, equivalent to a pressure of one atmosphere, applied to the piston is 1·38 mm. The period of the indicator is 1/250-sec.

The graphs produced by the scribing style on the smoked-paper chart (which receives also a record of the time of passage of the secondary discharge spark used to ignite the mixtures and the trace of an electrically driven tuning-fork making fifty vibrations per second) are measured, after fixation of the chart in a bath of weak spirit varnish, by the aid of a specially designed apparatus (see "Record of First Series of the British Coal Dust Experiments," p. 75, London, 1910), consisting essentially of a microscope with fine cross-wires in the eyepiece and a drum mounted on V-supports in which it can rotate or slide laterally. The circumference of the drum is divided into millimetres and rests against a vernier, whilst lateral movement of the drum is measured by means of a micrometer screw with a divided head.

Method of Conducting an Experiment.—The sphere having been assembled, it was exhausted of air to within a few mm. of mercury by means of a Gaede mercury pump, and the mixture to be experimented with introduced. Each mixture was prepared in an 18-litre glass gas-holder over glycerol and water, well shaken, and allowed to remain during six hours, and analysed before use. The secondary discharge used to ignite the mixtures was obtained from a "10-inch" *X*-ray coil by breaking a current of 10 amperes in the primary circuit, the trembler being locked. The discharge passed across a 10 mm. gap at the centre of the sphere, and simultaneously a record of its passage was made on the smoked-paper chart on the revolving drum.

Speed of Propagation of Flame.—Measurements of the speeds of propagation of flame were obtained for a series of mixtures by recording the time of passage of the secondary discharge used to ignite them at the centre of the vessel and the time at which short screen wires of copper 0·025 mm. in diameter, stretched at a distance of 7·5 cm. vertically above and below the point of ignition, were melted. The screen wires carried an electric current of 0·5 ampere at 4 volts and were in series with the electromagnets of delicate Deprez indicators, the latency or "time-lag" of which was found to be negligible. (The armatures, carrying aluminium styles for recording on the smoked-paper chart, moved freely with a current of 0·1 ampere at 1 volt.)

Calculation of Theoretical Maximum Pressures.—For the purpose of calculating the theoretical maximum pressures that should be given by the different mixtures, it was necessary to obtain information as to the proportion of the methane completely burned to form carbon dioxide and steam at the time of attainment of maximum pressure, more particularly in those mixtures containing excess of methane. To this end, a series of experiments was made

in which a capillary tube of copper, fitted with a tap, was fixed through the side of the 4-litre sphere (in place of the quartz window). The tube projected 4·8 cm. within the sphere (that is, midway between the centre and the circumference), and outside the sphere, beyond the tap, it was bent so as to dip below the surface of mercury in a trough. A gas-collecting tube of 25 c.c. capacity, filled with mercury, was inverted in the trough over the end of the bent tube.

The sphere was filled with the inflammable mixture in the usual manner, enough gas passed through the copper delivery tube to displace the air therein, and the tap closed. The mixture having been ignited, the tap was opened at the moment of attainment of maximum pressure by revolving it rapidly through 180 degrees. During the short time that the tap was thus opened, the pressure within the sphere forced out into the collecting tube between 5 and 10 c.c. of the products of combustion, a quantity sufficient for accurate analysis.

The results of the analyses, after making a correction for the unburnt mixture contained in the capillary tube, were as follow:

Methane in original mixture.	Analysis of products of combustion.				
Per cent.	CO_2.	O_2.	CO.	H_2.	CH_4.
7·90	9·25	3·82	0·15	nil	nil
9·40	11·14	0·74	0·26	nil	nil
9·90	10·66	0·13	1·12	0·40	0·24
10·00	10·86	0·04	1·08	0·68	0·04
10·70	9·04	nil	3·63	2·21	0·10
11·05	9·00	nil	3·44	1·95	0·23
12·10	8·09	0·07	5·85	4·00	0·07
12·90	6·08	0·05	7·78	6·73	0·36
13·90	5·45	nil	8·95	9·45	1·00
14·70	4·13	nil	9·85	11·15	0·61

These results should be compared with similar analyses of "flame gases" obtained during the propagation of flame in upper limit mixtures with air and with mixtures of oxygen and nitrogen containing less oxygen than air (T., 1914, **105**, 2596). The percentages of the total methane in the original mixtures burnt to form carbon dioxide and steam are plotted against the ratios O_2/CH_4 in the original mixtures in Fig. 7, which includes also the results obtained with the upper limit mixtures. From the curve so obtained, it is possible to estimate for any mixture of methane and air, with sufficient accuracy for the calculation of the heat developed, the proportions in which the reactions:

$$CH_4 + 2O_2 = CO_2 + 2H_2O + 191{,}070 \text{ calories} \quad . \quad . \quad . \quad . \quad (1)$$

$$CH_4 + O_2 = CO + H_2 + H_2O + 65{,}760 \text{ calories} \quad . \quad . \quad . \quad . \quad (2)$$

can be assumed to have taken place during combustion.

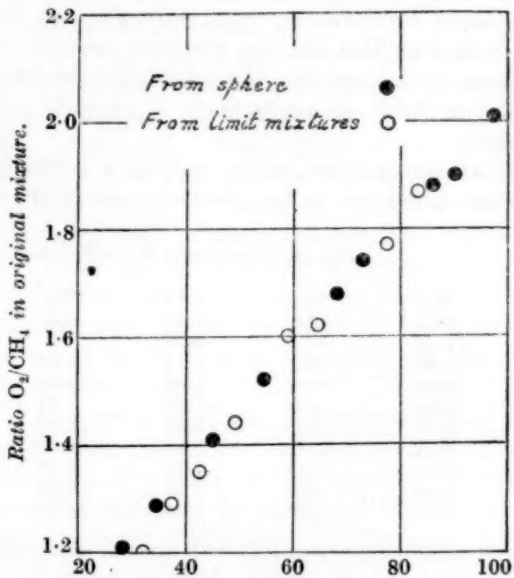
The calculation is as follows. The mixtures being saturated with water vapour at 15°, the original pressure of the mixture is 0·983 atmosphere, with 0·017 atmosphere of water vapour. The final pressure, if the gases are cooled to 15° without condensation of steam, is equal to the original pressure plus the partial pressure of any methane burnt according to equation (2).

Let Q be the heat of the reaction, then

$$Q = p\mathrm{CH}_4(aq + bq'),$$

where $p\mathrm{CH}_4$ is the partial pressure of the methane burnt (corrected

FIG. 7.



for the presence of water vapour), a and b represent the proportions burnt according to equations (1) and (2) respectively, and q and q' the corresponding heats of combustion.

The rise of temperature, t, is given by the equation

$$t = \frac{p\mathrm{CH}_4(aq+bq')}{(p\mathrm{H}_2+p\mathrm{O}_2+p\mathrm{N}_2+p\mathrm{CO})(4{\cdot}8+0{\cdot}0006t)+p\mathrm{CO}_2(6{\cdot}7+0{\cdot}0026t)+p\mathrm{H}_2\mathrm{O}(5{\cdot}9+0{\cdot}00215t)}.$$

Where unburnt methane remains in the mixture a term for the specific heat of methane, appropriate to the temperature, requires to be introduced in the denominator on the right-hand side of the equation.

The absolute pressure, P, is given, in atmospheres, by the equation

$$P = \frac{t+288}{288}(p + p\mathrm{CH}_4 \cdot b).$$

The majority of the experiments described in this paper were carried out during the winter of 1912 with the assistance of Mr. M. J. Burgess. For the experiments on the speeds of propagation of flame, as well as for assistance in checking some of the earlier results, I am indebted to Mr. W. Mason.

ESKMEALS,
CUMBERLAND.

[*Received, August 12th*, 1918.]

LXXVIII.—*A Synthesis of* iso*Brazilein and Certain Related Anhydropyranol Salts. Part I.**

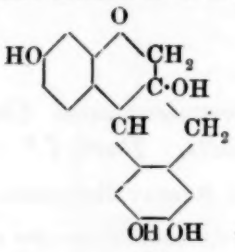
By HERBERT GRACE CRABTREE and ROBERT ROBINSON.

ALTHOUGH accumulated evidence decisively establishes the constitution of brazilin, it must be admitted that the necessary arguments are somewhat intricate, and consequently the problem of the synthesis † of the substance and its more important derivatives

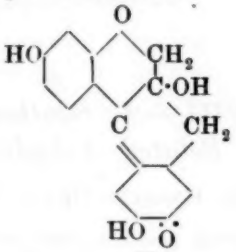
* The original intention of the authors to publish this research as a single communication has been revised in view of the very considerable delay which has been caused by their inability to complete the experimental work under existing conditions. They have reserved for Part II. a description of the homologues of the methylated *iso*brazilein salts, and also the intermediate product in the synthesis and the identification of the synthesised *iso*brazilein with that obtained from brazilin. It is hoped that the method of synthesis of *iso*brazilein may prove applicable also to the synthesis of *iso*hæmatein.

† Pfeiffer and Grimmer in a communication (*Ber.*, 1917, **50**, 911) bearing the rather misleading title, "The Brazilin Question," have announced their intention of attacking the problem of the synthesis of brazilin and its derivatives, but are apparently unaware that the method they propose to employ has already been indicated by Perkin and Robinson (P., 1912, **28**, 7). The former authors have so far obtained 3-anisylidene-7-methoxy-2 : 3-dihydro-1 : 4-benzopyrone, whereas the latter prepared a nearer relative of brazilin, namely, 3-veratrylidene-7-methoxy-2 : 3-dihydro-1 : 4-benzopyrone, and stated that they had made observations indicating the probability that the substance could be converted into a derivative of brazilin. This veratrylidene compound was later prepared in larger amount and in a purer condition, and the research was elaborated in various directions, although a number of circumstances have combined to retard the completion of the work. There has, however, never been any intention of abandoning a line of investigation which has always been regarded as likely to lead to a synthesis of trimethylbrazilin.—W.H.P., R.R.

retains considerable interest. Perkin and Robinson (T., 1908, **93**, 515) have already synthesised brazilinic acid and the lactone of dihydrobrazilinic acid, substances containing all the carbon atoms of brazilin, but in which the chromane and hydrindene rings are ruptured as the result of oxidation. Up to the present, no brazilin derivative has been synthesised that contains the characteristic fused ring system of the parent compound, nor does this skeleton occur in the molecule of any substance not itself obtained from brazilin or hæmatoxylin. We are now able to describe a simple method of synthesis of the *iso*brazilein salts, a result which harmonises with previous work and confirms the correctness of the view that brazilin is to be represented by the formula I.



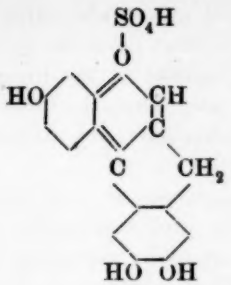
(I.)



(II.)

As is well known, brazilin, $C_{16}H_{14}O_5$, is converted by oxidation into the quinone brazilein, $C_{16}H_{12}O_5$ (II), and the latter was found by Hummel and A. G. Perkin (T., 1882, **41**, 367) to be transformed by mineral acids into a series of bright, orange-red salts which were called the *iso*brazilein salts. *iso*Brazilein hydrogen sulphate has the composition $C_{16}H_{11}O_4 \cdot HSO_4$. Subsequently, these derivatives were examined by Engels, Perkin, and Robinson (T., 1908, **93**, 1121), who devised methods for the preparation of the methyl ethers of the salts and recognised the relation of the series to the anhydropyranol or pyrrylium oxonium salts. The constitutional formulæ III and IV were assigned to *iso*brazilein hydrogen sulphate and to the trimethyl ether of *iso*brazilein ferrichloride * respectively (*loc. cit.*).

* Engels, Perkin, and Robinson (*loc. cit.*) did not give names to these ethers which could be used to show their relation to brazilin. The difficulty is that *iso*brazilein, which is really *anhydro*brazilein and a quinone, contains only two hydroxyl groups and can yield only a dimethyl ether. The formation of a salt produces a further hydroxyl group from the quinonoid oxygen above, and it is possible to have a trimethyl ether of the salts. For this reason it is necessary to speak of *iso*brazilein ferrichloride trimethyl ether, and not of, what at first sight appears more natural, trimethyl*iso*brazilein ferrichloride. The systematic names are very cumbrous, the salt in question being 4 : 7 : 5′-trimethoxy-4 : 3-indeno-1 : 4-benzopyranol anhydroferrichloride.



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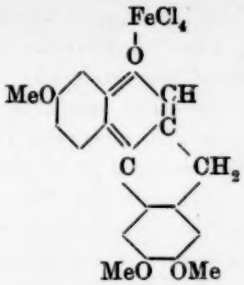
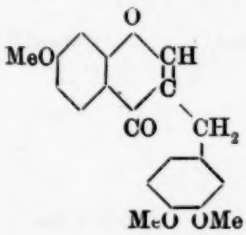
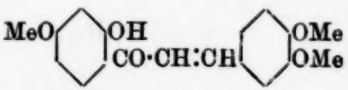


(IV.)

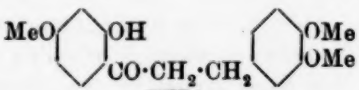
Now, these particular derivatives of brazilin were obviously suitable objects of a synthetical investigation, partly on account of the vivid fluorescence which they exhibit under appropriate conditions, rendering the formation of a mere trace detectable, and also because the pyrrylium nucleus may be produced by the application of widely differing methods. We thought it very probable that the chromone derivative, V, would be converted into the trimethyl ether of an *iso*brazilein salt by the condensing action of acidic dehydrating agents, and our first attempts were accordingly directed towards the preparation of this substance by a method similar to that which had been employed for the synthesis of another 3-substituted chromone, namely, anhydrobrazilic acid (Perkin and Robinson, T., 1908, **93**, 504). Butein trimethyl ether (VI) (A. G. Perkin and Hummel, T., 1904, **85**, 1468) was obtained by the condensation of paeanol and veratraldehyde and reduced by the catalytic method to its dihydro-derivative (VII), but all attempts to convert this subsance into a pyrone by condensation with ethyl formate or ethyl oxalate by means of sodium or analogous agents were unsuccessful. It was observed, however, that the ketone, VII, exhibited a tendency to produce highly



(V.)



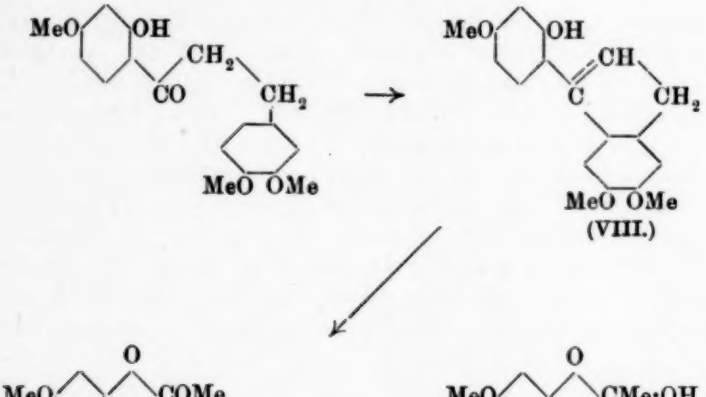
(VI.)



(VII.)

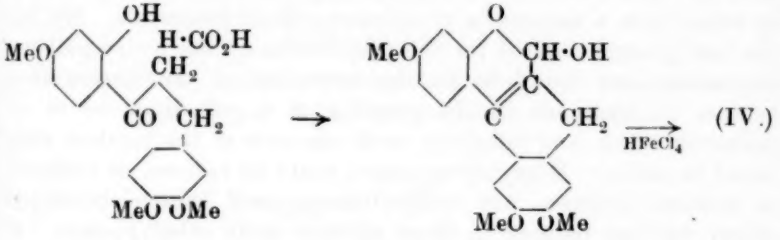
fluorescent substances when heated with acid anhydrides, and by boiling acetic anhydride in the presence of zinc chloride it was completely converted into an oxonium salt isolable in the form of its ferrichloride, and this product closely resembled the brazilin derivative, IV, especially in regard to the characteristic uranium-green fluorescence of its dilute aqueous solution.

The conclusion that the substance is a homologue of *iso*brazilein ferrichloride trimethyl ether was supported by analytical data, and a whole series of similar salts may be obtained by replacing the acetic anhydride by other anhydrides. The synthesis probably occurs as represented below, but it is impossible to decide without further evidence whether indene-ring formation or acetylation is the first stage in the process. The final product indicated is an α-pyranol, which is converted by the action of acids into an *anhydro*-salt containing the pyrrylium nucleus. In this connexion we have included on p. 874 an account of some experiments made in 1909 by Mr. M. R. Turner, in collaboration with one of us, which go to show that an identical salt is obtained by the action of acid on corresponding α- and γ-*pyranols*.



The action of dry hydrogen chloride, together with acetic anhydride and zinc chloride, on dihydrobutein trimethyl ether in the cold furnished a substance which is probably the indene derivative (VIII), and this is converted by the further action of hot

acetic anhydride and zinc chloride into the oxonium salt. The description of the foregoing compounds is reserved for a future communication. It was evident that in order to synthesise an *iso*brazilein salt, it would be necessary to introduce formic acid instead of acetic or other carboxylic acid in these reactions, and many attempts were made to utilise the mixed anhydride of formic and acetic acids in the hope that the phenol, VII, could be formylated and then further condensed in the desired direction. Unfortunately, this mixed anhydride, in the presence of salts such as zinc chloride or sodium acetate, or of acids or tertiary bases, decomposes too readily into carbon monoxide and acetic acid to be of great service as a reagent, and no progress was made along these lines. After numerous experiments in other directions, it was found that prolonged boiling of dihydrobutein trimethyl ether with a large excess of absolute formic acid and zinc chloride gave rise to a product from which *iso*brazilein ferrichloride trimethyl ether could be readily isolated. The synthesis is represented below:

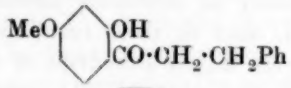


(IV.)

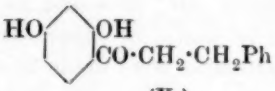
On heating the trimethyl ether salt* with hydrochloric acid at 150° in a sealed tube, a product was obtained which had all the reactions of *iso*brazilein hydrochloride. This demethylation will be further investigated if possible. The favourable issue of the research depended very largely on the devising of practical methods for the synthesis of hydrochalkone derivatives, and as a preliminary the processes available for the preparation of 2-hydroxy-4-methoxyphenyl phenylethyl ketone (IX) were compared. Bargellini and Marantonio (*Gazzetta*, 1908, **38**, ii, 514) obtained the corresponding dihydric phenol, 2:4-dihydroxyphenyl phenylethyl ketone (X), by the condensation of β-phenylpropionic acid with resorcinol by means of zinc chloride at 140—150°, and gave

* Before carrying out the demethylation, the ferric chloride was removed from the substance by conversion through the sparingly soluble orange-red sulphate into the hydrochloride. The sulphate was obtained by gently warming the ferrichloride with concentrated sulphuric acid and pouring into water. The process was repeated, and the hydrochloride obtained from the sulphate by the action of aqueous-alcoholic hydrochloric acid.

conditions under which it was claimed that it could be converted into either a monomethyl ether melting at 74—75° or a dimethyl ether melting at 103—104°.



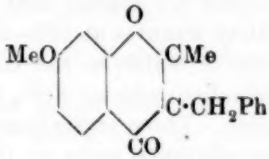
(IX.)



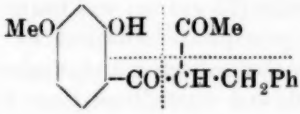
(X.)

As the result of our experiments, we are forced to the conclusion that the monomethyl ether melting at 74—75° does not exist, and that the so-called dimethyl ether is really the monomethyl ether. This substance crystallises from alcohol in needles melting at 105°; it contains only one methoxyl group, and may be obtained either by the methylation of the ketone, X, or by the reduction of benzylidenepaeanol. Its alcoholic solution gives a reddish-violet coloration with ferric chloride, but the phenolic function is weak, and the sodium salt is hydrolysed by water to such an extent that the substance may be completely extracted by ether from a suspension in aqueous sodium hydroxide. By far the best general method for the preparation of the hydrochalkone derivatives was found to be the reduction of the unsaturated ketones by hydrogen in the presence of a palladium sol or of palladium-black, and relatively small amounts of the catalyst were found to suffice. Benzylidenepaeanol could be reduced in alcoholic or ethereal solution, but veratrylidenepaeanol (butein trimethyl ether) was not reduced in those solvents or in ethyl acetate. It was, however, readily attacked in acetic acid solution. In the course of preliminary experiments we obtained one substance constituted similarly to the chromone, V. Kostanecki and Różycki (*Ber.*, 1901, **34**, 102) have shown that the acetylation of resacetophenone and of paeanol under correct conditions leads to the formation of chromone derivatives, and we have found that this reaction can be imitated in the case of benzylresacetophenone (X), but not with benzylpaeanol (IX). Acetic anhydride and sodium acetate at the boiling point of the mixture converts the former substance into the acetyl derivative of a hydroxybenzylmethylchromone, which is itself obtained on hydrolysis of the acetyl derivative, and may be converted in the usual manner into a methyl ether. The methyl ether is 7-methoxy-3-benzyl-2-methyl-1:4-benzopyrone (XI), as is proved by the fact that on hydrolysis by means of methyl-alcoholic potassium hydroxide it yields 2-hydroxy-4-methoxyphenyl phenylethyl ketone (IX), benzylacetone, and 2-hydroxy-4-methoxybenzoic acid. The formation of these substances is explicable as the result of the scission of the

primary product of hydrolysis (XII) in the two directions indicated by the dotted lines.



(XI.)

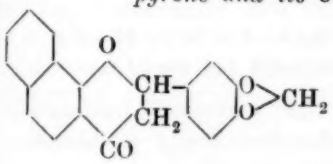


(XII.)

This chromone could not be converted into a salt of *iso*brazilein type, but many examples could be quoted to show that such an observation cannot safely be applied as a criterion of the probable behaviour of a corresponding veratryl derivative. The method which in this case was successfully used in the preparation of a 3-benzylchromone failed in the veratric series, because the condensation of resorcinol and 3:4-dimethoxyphenylpropionic acid in the presence of zinc chloride gave only tarry products.

Experimental.

3′:4′-Methylenedioxy-2-phenyl-2:3-dihydro-1:4-α-naphthapyrone and its 3-Piperonylidene Derivative.



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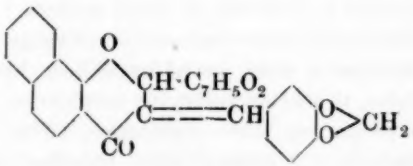


It has been pointed out on p. 861 that efforts were made to prepare 3-*homo*veratrylchromones, and among the possible methods seemed to be that depending on the realisation of the transference of a double bond in a veratrylidenechromanone from the *exo*cyclic to the *endo*cyclic position. As a preliminary case, the readily accessible substances figured above were prepared, but it was not found possible to convert the piperonylidene derivative into a true chromone by inducing a movement of the ethylene linking. Under varied treatment, the substance remained unchanged or suffered decomposition in other directions. The starting point in these experiments was 1-hydroxy-β-naphthyl methyl ketone

(2-acetyl-1-naphthol), and this was obtained by a slight modification of Friedländer's process (*Ber.*, 1895, **28**, 1946). An intimate mixture of α-naphthol (50 grams), acetic acid (75 grams), and zinc chloride (75 grams) was heated during thirty minutes at 160—170°. The precipitate obtained by the addition of water to the cooled mass was collected and washed with dilute hydrochloric acid, then dried, and crystallised from methyl alcohol. Three crystallisations gave a product melting at 99° (the pure substance melts at 103°), and this was sufficiently pure for most experiments. Our yield was always much diminished when we adopted the method of purification through the sodium salt, as recommended by Friedländer. Piperonylidenemethyl 1-hydroxy-β-naphthyl ketone (Kostanecki, *Ber.*, 1898, **31**, 707) was converted into the corresponding flavanone by a method similar to that frequently employed by Kostanecki and his co-workers. The unsaturated ketone (10 grams) was dissolved in hot alcohol (600 c.c.), and after the addition of concentrated hydrochloric acid (80 c.c.) and water (240 c.c.), the mixture was boiled under reflux during twenty-four hours. The solution was filtered hot, and, on cooling, the flavanone separated in pale orange needles, which were recrystallised from alcoholic hydrochloric acid, and then again twice from alcohol, when they were colourless and melted at 145°:

0·2460 gave 0·6792 CO_2 and 0·0974 H_2O. C = 75·3; H = 4·4.
$C_{20}H_{14}O_4$ requires C = 75·5; H = 4·4 per cent.

The substance is sparingly soluble in light petroleum, moderately so in methyl or ethyl alcohol, and dissolves freely in benzene, chloroform, acetone, or ethyl acetate.

Piperonylidene Derivative.—Owing to the ease with which the flavanone is reconverted by sodium hydroxide into the unsaturated ketone, it was necessary to employ an acid as the condensing agent in preparing this substance. The flavanone (2 grams) and piperonal (2 grams) were together dissolved in acetic acid (10 grams), and the solution was then saturated with hydrogen chloride. After allowing to remain overnight, the crystals which had separated were collected and crystallised from a mixture of nitrobenzene and alcohol. The substance was so obtained in rich golden balls of needles melting at 206°, and very sparingly soluble in most organic solvents:

0·1986 gave 0·5425 CO_2 and 0·0751 H_2O. C = 74·5; H = 4·2.
$C_{28}H_{18}O_6$ requires C = 74·7; H = 4·0 per cent.

The solution of this compound in sulphuric acid is intense reddish-purple. The nature of the dark green products obtained

by the action of vigorous acid condensing agents, such as phosphoryl chloride, could not be ascertained.

7-Hydroxy-3-benzyl-2-methyl-1 : 4-benzopyrone.

The acetyl derivative (see below) was boiled during two and a-half hours with an excess of dilute aqueous sodium carbonate, when it gradually dissolved as the result of hydrolysis. On cooling, the resulting phenol crystallised, and was collected and recrystallised from alcohol, being obtained in bundles of colourless, silky, prismatic needles melting at 282°:

0·1865 gave 0·5217 CO_2 and 0·0906 H_2O. C = 76·3; H = 5·4.

$C_{17}H_{14}O_3$ requires C = 76·6; H = 5·3 per cent.

The colourless solutions of the substance in cold aqueous sodium hydroxide or hot aqueous sodium carbonate exhibited violet fluorescence, and a similar appearance was obtained when the non-fluorescent solution in cold sulphuric acid was gently heated.

Acetyl Derivative.—2 : 4-Dihydroxyphenyl phenylethyl ketone (10 grams) was mixed with fused sodium acetate (15 grams) and acetic anhydride (20 grams), and heated in an oil-bath at 170° during four hours. Water and dilute hydrochloric acid were added to the cooled mass, and when the separated solid was free from acetic anhydride, it was collected, washed, dried, and crystallised from methyl alcohol, from which the compound separated in long, colourless needles melting at 121°:

0·2016 gave 0·5473 CO_2 and 0·0998 H_2O. C = 74·0; H = 5·5.

$C_{19}H_{16}O_4$ requires C = 74·0; H = 5·2 per cent.

The substance was not changed by dilute aqueous sodium hydroxide, and dissolved in sulphuric acid to a very pale yellow solution, which exhibited violet fluorescence on being heated.

Methyl Ether (XI).—7-Hydroxy-3-benzyl-2-methyl-1 : 4-benzopyrone (2 grams) was dissolved in hot methyl alcohol and mixed with methyl sulphate (5 c.c.). The solution was boiled under reflux, and aqueous potassium hydroxide (10 c.c. of 40 per cent.) gradually added during five minutes. The methyl ether was precipitated by the addition of water, but was not obtained in a satisfactory condition, and was therefore dissolved in ether, the ethereal solution washed with dilute sodium hydroxide, and dried. After the removal of the solvent, the oil solidified, and was crystallised from methyl alcohol, in which the substance is moderately readily soluble. The slender, colourless needles melted at 109°:

0·1675 gave 0·4722 CO_2 and 0·0859 H_2O. C = 76·9; H = 5·7.

$C_{18}H_{16}O_3$ requires C = 77·1; H = 5·7 per cent.

The solution in sulphuric acid is colourless and exhibits a faint blue fluorescence, which becomes intense on keeping or on gently heating, and this behaviour appears to be due to sulphonation. There was no evidence in numerous trials that the substance could be converted into a pyrrylium salt containing the indene nucleus.

Hydrolysis of the Methyl Ether.—A mixture of the methyl ether (1·5 grams), potassium hydroxide (2 grams), and methyl alcohol (10 c.c.) was heated in a wide test-tube in such a manner as gradually to remove a part of the methyl alcohol by distillation. A characteristic crimson coloration soon appeared and reached a maximum, after which it very quickly faded. When the solution or fusion had just lost the last trace of the red colour and had become yellow, the reaction was considered to be complete, and the mixture, together with the methyl-alcoholic distillate, was submitted to distillation in a current of steam. The aqueous distillate had the odour of benzylacetone, and the semicarbazone of the latter was prepared from it. This substance crystallised from alcohol in slender, colourless needles melting at 145° (Klages, *Ber.*, 1904, **37**, 2313, gives 142°), and at the same temperature when mixed with a purified specimen of the semicarbazone obtained from benzylacetone prepared by the reduction of phenyl styryl ketone by hydrogen in the presence of palladium. The alkaline solution remaining in the flask was rendered acid by the addition of hydrochloric acid, and then alkaline again with sodium carbonate. The oil precipitated by the acid did not redissolve, but soon solidified and was collected and crystallised from methyl alcohol, when it was obtained in colourless needles melting at 105°, and at the same temperature when mixed with a specimen of 2-hydroxy-4-methoxyphenyl phenylethyl ketone. The aqueous solution from which this substance had been separated was extracted with ether in order to remove further traces of the same compound; it was then concentrated and acidified, when a small amount of slender needles separated. The substance gave an intense violet colour with ferric chloride in aqueous solution, and melted at 155°. The melting point was not depressed when the substance was mixed with 2-hydroxy-4-methoxybenzoic acid obtained by the methylation of β-resorcyclic acid.

Methylation of Resacetophenone.

The following is a brief account of our observations in this connexion. The methylation to paeanol is advantageously effected by means of methyl iodide and potassium hydroxide in boiling methyl-alcoholic solution, and 10 per cent. more than the theoretically

required amount of each reagent suffices. If for each molecular proportion of resacetophenone three molecular proportions of methyl iodide and potassium hydroxide are employed, the main product is the dimethyl derivative, melting at 83—84° (Gregor, *Monatsh.*, 1894, **15**, 437; Wechsler, *ibid.*, **15**, 239; A. G. Perkin, T., 1895, **67**, 996), which has one of the methyl groups in the aromatic nucleus. An attempt was made to divide the operation of methylation into two parts, that is, to methylate first to paeanol and then to attempt the further conversion of this ether into the substance melting at 83—84°. When, however, paeanol was treated with two molecular proportions of methyl iodide and potassium hydroxide in boiling methyl alcohol, the greater part of the substance was recovered unchanged, and the small yield of product insoluble in cold sodium hydroxide solution was a mixture of about equal proportions of dimethylresacetophenone (m. p. 83—84°) and the normal dimethyl ether. The two substances could be separated by means of warm dilute sodium hydroxide, in which the former dissolves. This rather unexpected result renders it clear that the *C*-methylation of resacetophenone precedes the *O*-methylation in the case where an excess of methyl iodide and potassium hydroxide is employed. Probably the explanation is that, in the case of the dipotassium salt, methylation occurs at the carbon atom, whereas in the case of the monopotassium salt the *O*-ether is formed. If methyl sulphate is employed for the methylation, it is difficult to obtain a satisfactory yield of paeanol, and the substance melting at 83—84° is not obtained, but, instead, the normal dimethyl ether of resacetophenone.

A simple qualitative test which may be used to indicate the presence or absence of the nuclear methyl group in resorcinol derivatives of the type of resorcylic acid or resorcinol ketones depends on the formation of homofluorescein or fluorescein respectively. The substance is strongly heated with an excess of phthalic anhydride and a few drops of sulphuric acid, and the product dissolved in dilute sodium hydroxide. Fluorescein is formed under these conditions from most resorcinol derivatives, even if they are alkylated at the oxygen atom and the appearance of the alkaline solution is well known. If the resorcinol nucleus contains the methyl group, however, the alkaline solution is intense cherry-red, and the fluorescence is less persistent on dilution than is the case with fluorescein itself.

2-Hydroxy-4-methoxyphenyl Phenylethyl Ketone (IX).

We have carefully repeated the work of Bargellini and Marantonio (*loc. cit.*) on the methylation of 2:4-dihydroxyphenyl phenylethyl ketone, and have failed to obtain the so-called monomethyl ether melting at 74—75°. On the other hand, the prescription given for the preparation of the dimethyl ether works well, and the product is the real monomethyl ether. The substance crystallised from alcohol in colourless needles melting at 105°:

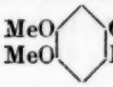
0·1635 gave 0·4491 CO_2 and 0·0927 H_2O. C = 74·9; H = 6·3.
0·4126 „ 0·3690 AgI. MeO = 11·9.
$C_{16}H_{16}O_3$ requires C = 75·0; H = 6·3; MeO = 12·1 per cent.

The same substance was obtained by the methylation of 2:4-dihydroxyphenyl phenylethyl ketone by means of half the theoretical amount of methyl sulphate, and also by employing methyl iodide. It was insoluble in aqueous sodium carbonate or sodium hydroxide in the cold, but dissolved in the latter on heating. It gives an intense reddish-violet coloration on the addition of ferric chloride to its alcoholic solution. Attempts to convert the substance into definite acetyl or benzoyl derivatives were unsuccessful, and we were unable to obtain its methyl ether. The constitution of the compound is best demonstrated by the following method of preparation.

Benzylidenepaeanol (Emilewicz and Kostanecki, *Ber.*, 1899, **32**, 312) could be reduced by hydrogen in the presence of palladium in ethereal or alcoholic solution, but the latter was more convenient in practice. The chalkone (5 grams) was dissolved in ethyl alcohol (250 c.c.) at from 50—60°, and the air in the flask containing the solution was then expelled by purified hydrogen, after which palladous chloride solution (15 c.c. of 1 per cent.) and gum arabic (15 c.c. of 1 per cent. solution) were added. The flask was then closed, vigorously shaken by mechanical means, and connected to the hydrogen generator.

The reduction proceeded rapidly and could easily be followed by noting the rapidity of the stream of hydrogen which passed through the wash-bottles. After twenty minutes, the gas was no longer absorbed, and this was coincident with the disappearance of the yellow colour of the alcoholic solution. The greater part of the alcohol was removed from the filtered solution by distillation, and, on cooling, the concentrate deposited 4·8 grams of needles melting at 105°. The substance melted at the same temperature when intimately mixed with a specimen obtained by the methylation of 2:4-dihydroxyphenyl phenylethyl ketone.

6-Bromo-3:4-dimethoxy-β-phenylpropionic Acid,



The condensation of 3:4-dimethoxyphenylpropionic acid and resorcinol in the presence of zinc chloride did not give useful results, probably owing to the ease with which the acid undergoes internal dehydration with the formation of dimethoxyhydrindone. It was thought that the bromo-acid would be more amenable in this reaction, but such did not prove to be the case.

3:4-Dimethoxyphenylpropionic acid was brominated in cold acetic acid solution by means of a molecular proportion of bromine dissolved in the same solvent. A part of the product crystallised and the remainder was obtained on the addition of water. The substance was crystallised from aqueous acetic acid and obtained in clusters of needles melting at 123°:

0·0916 required for neutralisation 0·01778 KOH.

This amount of a monobasic acid, $C_{11}H_{13}O_4Br$, requires 0·01772 KOH.

This acid is converted by phosphoric oxide in boiling benzene solution into a hydrindone derivative, which yields a very sparingly soluble piperonylidene derivative.

2-Hydroxy-4-methoxyphenyl 3:4-Dimethoxyphenylethyl Ketone (Dihydrobutein Trimethyl Ether), VII.

Veratrylidenepaeanol (A. G. Perkin and Hummel, *loc. cit.*) was found to be more difficult to reduce than the benzylidene derivative, and ether, alcohol, and ethyl acetate were all found to be unsuitable solvents. Ultimately, acetic acid was successfully employed, and the addition of a protective colloid, such as gum arabic, was omitted. The chalkone (5 grams), dissolved in acetic acid (450 c.c.), heated to 70—80°, was reduced by shaking with hydrogen after the addition of palladous chloride solution (20 c.c. of 1 per cent.). The absorption of gas slackened after half an hour, but, as the reaction did not appear to be complete, the liquid was again heated to 70—80° and 10 c.c. of the palladous chloride solution were added. The reduction was then completed by shaking with hydrogen for an hour. The colourless solution was filtered from the palladium-black and the acetic acid recovered by distillation under diminished pressure. Brine was added to the residue, and the colourless solid which was precipitated was collected, washed with water, and crystallised from methyl alcohol.

The substance crystallised in stout, colourless prisms melting at 84°, and the yield was 80 per cent. of that demanded by theory:

0·1400 gave 0·3512 CO_2 and 0·0879 H_2O. C = 68·4; H = 6·5.

$C_{18}H_{20}O_5$ requires C = 68·4; H = 6·3 per cent.

The coloration in alcoholic solution produced by the addition of a drop of ferric chloride is almost identical with that obtained in the case of ethyl acetoacetate. The substance is converted by dilute aqueous sodium hydroxide into a very sparingly soluble, voluminous sodium salt, but this is decomposed in the presence of ether, which extracts the free enol.

Synthesis of iso*Brazilein Ferrichloride Trimethyl Ether.*

A mixture of the compound just described (3 grams), fused zinc chloride (5 grams), and anhydrous formic acid (20 grams) was boiled for three hours under reflux. After a short time, the solution assumed a red colour and green fluorescence, and this became much intensified as the reaction proceeded. After cooling, dilute hydrochloric acid and an excess of concentrated ferric chloride solution were added, and a dark brown, viscid mass was precipitated. This was collected, freed as far as possible from adhering liquid, and then dissolved in hot acetic acid. As the solution cooled, pale brown, glistening needles with metallic glance separated, which were collected and purified by recrystallisation from acetic acid. Half a gram of the pure substance was obtained. In some respects, this synthesised material did not appear to be identical with *iso*brazilein ferrichloride trimethyl ether, which, as usually obtained (Engels, Perkin, and Robinson, *loc. cit.*, p. 1151), crystallises in magnificent copper leaflets, and it seemed at first sight necessary to conclude that the two substances were different. The reactions of the two specimens were, however, very similar, except with dilute aqueous sodium hydroxide, which in the case of the copper leaflets developed a reddish-purple colour. From previous experience, we surmised that this reaction must be due to the presence of phenolic groups, since the pyranol bases from methoxyanhydropyranol salts are colourless and insoluble in alkaline solutions. Since, in addition, microscopic examination of the copper leaflets showed that the crystals had curved edges, it became very probable that the substance obtained from brazilin was contaminated with a small proportion of a demethylated salt, the result of the action of the concentrated sulphuric acid used in the operation. This view was proved to be correct, since by exercising great care in the preparation we obtained the salt from brazilin in the same crystalline form as characterised the synthesised speci-

men. The tetramethyldihydrobrazileinol employed in the preparation was repeatedly purified by solution in light petroleum, as described by Engels, Perkin, and Robinson (*loc. cit.*), and ground in a mortar with excess of cold sulphuric acid for only ten minutes. The sulphate and hydrochloride were then isolated as already described, and the anhydroferrichloride was prepared from the latter in hot aqueous-alcoholic hydrochloric acid solution. The precipitated salt was recrystallised from acetic acid, and in this way a specimen was obtained which was identical in all respects with the material synthesised in the manner described above. The whole of the following observations were made with both specimens, and the two experiments carried out side by side and as nearly as possible under the same conditions. In all cases, complete identity of behaviour was recorded; all the colours appeared at the same stage; turbidity, fluorescence, and behaviour on dilution were always the same. The crystals are well-defined, pointed needles, transparent under the microscope, and in mass are pale ochreous-brown and have a coppery lustre. A suspension of the crystals in acetic acid has a characteristic appearance. If crystallised rapidly by cooling a concentrated solution in hot acetic acid, the tendency is for two or three needles to form a cluster, and at the ends of each of the larger needles a great number of very small needles collect. The substance has no definite melting point, it darkens at 180°, and above this temperature decomposition is progressive; from 203° to 215° there was shrinking and melting accompanied by decomposition. On breaking the capillary tubes, the contents were greenish-black and had a green lustre. The solubility of the substance in various solvents was noted. It does not dissolve in alcohol in the cold to any appreciable extent; on warming, the alcohol acquires an apple-green fluorescence, and, on boiling, the fluorescence is intense ivy-green and the solution becomes yellowish-brown. An aqueous solution of the substance is at first yellow and exhibits brilliant green fluorescence. On keeping, the salt is hydrolysed and the solution becomes slightly milky, the original appearance being restored by the addition of a few drops of hydrochloric acid. 0·1 Gram dissolves to a clear solution in 100 c.c. of water with the addition of 0·5 c.c. of concentrated hydrochloric acid. The behaviour of this solution on dilution was noted, and the fluorescence was found to be remarkably persistent. The addition of sodium acetate to the aqueous solution destroyed the fluorescence, and the pyranol base could be extracted by ether. The ethereal layer was very pale yellow, and the yellow, strongly fluorescent hydrochloride was regenerated by washing it with dilute hydrochloric acid. On the addition of nitric acid to the solution

of the substance in water, the first appearance was the loss of fluorescence and the production of a bright cherry-red colour. On keeping, the colour became yellow, and the fluorescence reappeared and was even more intense than that of the original solution. On the addition of sodium hydroxide to a solution of the ferrichloride, a faint cherry-red opalescence resulted; on shaking with air, a brownish-red solution and precipitate were obtained.

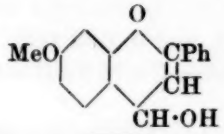
Appendix I.

Some Anhydropyranol Salts.

By Robert Robinson and Maurice Russell Turner.

About ten years ago the authors carried out a series of experiments in the benzopyranol group with the object of determining the nature of the pyranol bases and of discovering the cause of the intense colour which characterises some of these substances. It was found that the coloured pyranol bases are all quinones occasionally retaining tenaciously a molecule of water, and thus appearing to be carbinols. Several of these quinones were isolated in a pure condition, and it is hoped at some future time to publish an account of the investigation. In order to prove that the true carbinols are colourless, we prepared methyl ethers, and it is in connexion with these substances that certain points were noted which are of interest in relation to the foregoing communication. It is especially interesting that anhydro-salts of 7-methoxy-2-phenyl-1:4-benzopyranol (XIII) and of 7-methoxy-2:4-diphenyl-1:4-benzopyranol (XIV) dissolve in water with an intense bluish-green fluorescence, and in this respect closely resemble the similarly constituted *iso*brazilein hydrochloride trimethyl ether, but, on the other hand, differ from related hydroxy-compounds. The former substance (XIII) was obtained by the application of the general method for the preparation of anhydropyranol salts devised by Perkin, Robinson, and Turner (T., 1908, **93**, 1115), namely, by the condensation of 2-hydroxy-4-methoxybenzaldehyde with acetophenone in acetic acid solution by means of hydrogen chloride. The second compound (XIV) was obtained by the condensation of dibenzoylmethane with the monomethyl ether of resorcinol in the presence of sulphuric acid, but it was found impossible to obtain it by this method free from the corresponding demethylated compound, and the benzopyranol prepared from the salt was always red. This method of preparation has already been described by Becker and Decker (*Ber.*, 1914, **47**, 2288).

In order to obtain the substance in a pure condition, three methods could be employed, and are described on p. 877. As was to be expected, the compound (XIV) may be prepared by the action of magnesium phenyl bromide on 7-methoxy-2-phenyl-1 : 4-benzopyrone (XV), and was isolated from the product in the form of the anhydroferrichloride melting at 185°. The same anhydroferrichloride was, however, obtained from the product of interaction of magnesium phenyl bromide and β-phenylumbelliferone methyl ether (XVI). This would seem to demonstrate the possibility of the existence of two carbinol bases corresponding with a single anhydro-oxonium salt, since the process last mentioned should lead to the α-pyranol (XVII).



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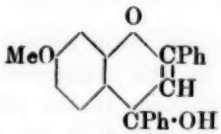

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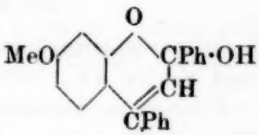

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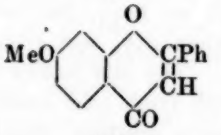

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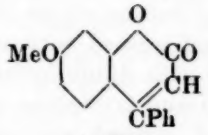


(XVI.)

EXPERIMENTAL.

7-Methoxy-4-phenyl-1 : 2-benzopyrone (β-Phenylumbelliferone Methyl Ether), XVI.

A. A mixture of resorcinol monomethyl ether (13 grams) and ethyl benzoylacetate (20 grams) was dissolved in ice-cold sulphuric acid (200 grams). The flask was immersed in melting ice and allowed to remain for twelve hours. The viscid product obtained by dilution with water was well washed, and became solid in con-

tact with a little alcohol. The substance was collected and recrystallised from alcohol.

B. β-Phenylumbelliferone was methylated in the usual manner in methyl-alcoholic solution by means of methyl sulphate and potassium hydroxide. At the end of the reaction, however, an excess of hydrochloric acid was added and the solution boiled in order to convert into lactone any hydroxy-acid which had been formed as the result of the hydrolysing action of the alkali. After the addition of water, the substance was collected and crystallised from alcohol; it is moderately readily soluble in alcohol or benzene, and crystallises in slender needles which melt at 110°. The pale yellow solution in sulphuric acid exhibits intense bluish-violet fluorescence:

0·1255 gave 0·3489 CO_2 and 0·0560 H_2O. C = 75·8; H = 4·9.
$C_{16}H_{12}O_3$ requires C = 76·2; H = 4·7 per cent.

2:4-Dimethoxydibenzoylmethane and 7-Methoxy-2-phenyl-1:4-benzopyrone (XV).

2:4-Dimethoxydibenzoylmethane has already been obtained by Perkin and Schiess (T., 1904, **85**, 164) by the condensation of methyl 2:4-dimethoxybenzoate with acetophenone in the presence of metallic sodium. Since, however, we happened to be in the possession of large quantities of 2:4-dimethoxyacetophenone, we employed this compound as the starting point. 2:4-Dimethoxyacetophenone (55 grams) and ethyl benzoate (90 grams) were dissolved in dry ether (250 c.c.), and powdered sodamide (50 grams) was gradually added to the solution. A vigorous reaction ensued and the colourless sodium salt of the diketone separated as a crust. After gently boiling under reflux for half an hour, the salt was separated and washed with ether, and, when dry, was triturated in a mortar with dilute hydrochloric acid. The oily product soon became solid and crystalline in contact with fresh cold water, and was collected, washed with sodium carbonate solution, dried, and crystallised from light petroleum. The pale yellow needles melted at 57°:

0·1403 gave 0·3683 CO_2 and 0·0758 H_2O. C = 71·6; H = 6·0.
$C_{17}H_{16}O_4$ requires C = 71·8; H = 5·6 per cent.

When this diketone is mixed with ten times its weight of hot hydriodic acid (D 1·9), an immediate reaction occurs, methyl iodide is evolved, and the flavone derivative separates. The process is remarkably smooth. After removing the free iodine by the addition of sulphurous acid, the precipitate was collected and crystallised from alcohol. It melts at 110°, and is doubtless identical

with the compound obtained by Emilewicz and Kostanecki (*loc. cit.*) by the action of alkali on benzylidenepaeanol dibromide. The intensity of the blue fluorescence of the solution of this flavone in sulphuric acid is noteworthy.

7-Methoxy-2-phenyl-1 : 4-benzopyranol Anhydrohydrochloride. (Anhydrohydrochloride of XIII.)

2-Hydroxy-4-methoxybenzaldehyde (8 grams) and acetophenone (6 grams) were dissolved in glacial acetic acid (25 c.c.), and the solution was saturated with hydrogen chloride during an hour and a-half. The orange needles which separated were collected, and more of the substance was obtained by the addition of ether to the solution. The salt could be recrystallised from dilute hydrochloric acid, and, after being dried in the air, melted and decomposed at 102—103°:

0·1155 gave 0·2506 CO_2 and 0·0606 H_2O. C = 59·2; H = 5·8.
$C_{16}H_{13}O_2Cl,3H_2O$ requires C = 58·8; H = 5·8 per cent.

The substance dissolves in water to a yellow solution exhibiting a striking bluish-green fluorescence, extremely persistent on dilution.

7-Methoxy-2 : 4-diphenyl-1 : 4-benzopyranol and its Salts.

A. 7-Hydroxy-2 : 4-diphenyl-1 : 4-benzopyranol dimethyl ether (Bülow and Sicherer, *Ber.*, 1901, **34**, 2380) loses methyl alcohol on treatment with acids, and yields salts of the monomethylated pyranol. The ferrichloride was obtained in the usual manner, and crystallised from acetic acid in orange-yellow needles melting at 185°, and at the same temperature when mixed with the salt obtained as described under *B* and *C*. The fluorescence of the dimethyl ether in acetic or sulphuric acid solution is due to the conversion to an oxonium salt of the pyranol now under consideration.

B. β-Phenylumbelliferone methyl ether (2 grams) was dissolved in hot benzene (50 c.c.) and treated with a solution of magnesium phenyl bromide in ether until a test portion developed an intense bluish-green colour on the addition of an ethereal solution of *p*-benzoquinone. The mixture was then heated on the steam-bath for ten minutes, cooled, and decomposed with water. The benzene solution contained a substance which is probably an α-pyranol, and gave an oxonium salt on the addition of hydrochloric acid. In order to isolate this, the whole product was treated with dilute hydrochloric acid, and the separated yellow, aqueous layer mixed

with an excess of concentrated ferric chloride solution. The precipitated yellow ferrichloride was crystallised from acetic acid and obtained in orange needles melting at 185°.

C. 7-Methoxyflavone (4 grams) dissolved in benzene (150 c.c.) was mixed with an ethereal solution of magnesium phenyl bromide (from 1·8 grams of bromobenzene). A yellow precipitate was formed, and after gently heating on the steam-bath for fifteen minutes, the mixture was decomposed by dilute hydrochloric acid. A copious precipitate of the ferrichloride was obtained on the addition of ferric chloride to the aqueous layer, and the derivative was collected and crystallised from acetic acid. The orange-yellow needles melted at 185°:

0·1469 gave 0·2783 CO_2 and 0·0475 H_2O. C = 51·7; H = 3·6.
0·3600 „ 0·0572 Fe_2O_3. Fe = 11·1.

$C_{22}H_{17}O_2Cl,FeCl_3$ requires C = 51·7; H = 3·3; Fe = 11·0 per cent.

The pyranol itself and its derivatives could most conveniently be obtained by the method *A*.

7-Methoxy-2 : 4-diphenyl-1 : 4-benzopyranol.—Bülow and Sicherer's dimethyl ether was dissolved in dilute hydrochloric acid and the solution treated with sodium acetate. The almost colourless precipitate was amorphous, but was obtained in a pure condition by washing with water and drying in a vacuum over sulphuric acid. It melted at 55—57°:

0·1323 gave 0·3862 CO_2 and 0·0702 H_2O. C = 79·6; H = 5·9.
0·1962 in 19·9 benzene gave $\Delta^t = 0·153°$. M.W. = 322.
$C_{22}H_{18}O_3$ requires C = 80·0; H = 5·5 per cent. M.W. = 330.

Anhydrodihydrochloride.—Dry hydrogen chloride was passed through an ethereal solution of the pyranol. Bright yellow crystals melting at 121° separated, and were dried in a vacuum:

0·2264 gave 0·1576 AgCl. Cl = 17·2.
$C_{22}H_{18}O_2Cl_2,2H_2O$ requires Cl = 16·9 per cent.

Direct proof of the existence of the water of crystallisation was not obtained.

Anhydrohydrochloride.—The dihydrochloride was dissolved in hot dilute hydrochloric acid, and the solution, on cooling, deposited red needles melting indistinctly at about 80°:

0·2148 gave 0·0900 AgCl. Cl = 10·4.
$C_{22}H_{17}O_2Cl$ requires Cl = 10·2 per cent.

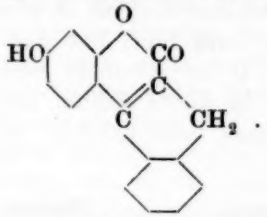
Anhydroplatinichloride.—This derivative was prepared in a hot solution, and crystallised, on cooling, in orange needles melting and decomposing at 224°:

0·2419 gave 0·0455 Pt. Pt = 18·8.

$(C_{22}H_{17}O_2Cl)_2PtCl_4$ requires Pt = 18·9 per cent.

Appendix II.

7-Hydroxy-4 : 3-indeno-1 : 2-benzopyrone,



This substance was prepared in 1911 by Mr. J. A. Prescott working in collaboration with one of us in the laboratories of the University of Manchester. Although the work was not carried far, it seems of interest to include a description of this substance in the present communication in view of the circumstance that it is the first compound to be synthesised the molecule of which contains the brazilin and hæmatoxylin skeleton.

α-Hydrindone (8·5 grams) dissolved in pure dry ether (100 c.c.) was converted into the sodium derivative by the addition of powdered sodamide (6 grams). The evolution of ammonia was facilitated by frequent shaking, and the reaction appeared to be complete in about two hours. A rather rapid stream of carbon dioxide was then passed through the solution until the ether had nearly all been removed by evaporation. Ice was then carefully added and the solution extracted twice with ether to remove a small amount of unchanged hydrindone. The separated aqueous layer was then acidified with hydrochloric acid with careful cooling by small pieces of ice. The crystalline precipitate was quickly collected and dried on porous porcelain. The yield of this *1-hydrindone-2-carboxylic acid* was 8 grams. The substance gives a reddish-violet coloration on the addition of ferric chloride to its aqueous or alcoholic solution. It is moderately stable at the ordinary temperature, but slowly decomposes with the formation of α-hydrindone and carbon dioxide. The reaction is rapid and complete on gently warming with water. The keto-acid (8·3 grams), together with resorcinol (9 grams), was mixed with a saturated solution (100 c.c.) of hydrogen chloride in methyl alcohol. The mixture was allowed to remain during two and a-half days at the ordinary temperature, when it became red, and a colourless substance crystallised. The liquid was then gently heated for two hours on the water-bath, and the quantity of the crystals was

increased. When cold, the substance was collected and crystallised from ethyl alcohol, from which it separated in colourless needles, the yield amounting to 2·1 grams:

Found: C = 76·4; H = 4·2.

$C_{16}H_{10}O_3$ requires C = 76·8; H = 4·0 per cent.

On heating, the substance darkens at about 230°, and at 280° rather suddenly turns dark blue, but does not melt at this or higher temperatures. It is sparingly soluble in most organic solvents, but dissolves in dilute sodium hydroxide. The solution in concentrated sulphuric acid exhibits an intense bluish-violet fluorescence.

UNIVERSITY OF LIVERPOOL. [*Received, September 23rd*, 1918.]

LXXIX.—*The Action of Chlorine on the Alkali Iodides.*

By WILLIAM NORMAN RAE.

IN a previous communication (T., 1915, **107**, 1286), an account was given of the action of bromine vapour on the solid iodides of the alkali metals, and the action of chlorine on the same compounds has now been studied.

The alkali metals form two series of polyhaloids containing both chlorine and iodine, having, respectively, the formulæ $MICl_2$ and $MICl_4$; all the compounds of the latter series were prepared in the wet way by Wells and Wheeler (*Amer. J. Sci.*, 1892, [iii], **44**, 42), who found that two of them gave hydrated crystals, namely, $LiICl_4,4H_2O$ and $NaICl_4,2H_2O$, whilst the others were anhydrous. The compounds $KICl_4$ and NH_4ICl_4 were originally prepared by Filhol (*J. Pharm.*, 1839, **25**, 435, 506).

In the present instance, the method of experiment was as follows: the iodides were powdered and kept in a desiccator over sulphuric acid for several weeks before using, to ensure thorough dryness; a small quantity was then placed in a weighing bottle having a ground-in glass stopper, through which passed two tubes, one of which reached nearly to the bottom of the bottle. During the weighings, the two tubes were closed with ground-in glass stoppers. Several of the bottles were connected in series, and a slow stream of chlorine, washed in water and dried with sulphuric acid, was passed through the train of bottles, and finally through

a calcium chloride tower, used to prevent moisture diffusing back in case the chlorine stream stopped. The bottles were weighed from day to day until the weight became constant, and the contents were then analysed. In all cases, the compound $MICl_4$ appeared to be formed. The compound $MICl_2$ for a given metal is much more stable than $MICl_4$, as is indicated by the well-marked breaks in the curves showing the loss of weight over potassium hydroxide with time, given in the previous paper (*loc. cit.*), and it might be expected that similar breaks would be obtained in the "increase of weight–time" curves in the present instance, the formation of the more stable compound $MICl_2$ proceeding more rapidly than that of the compound $MICl_4$. Such breaks, however, were not obtained, although there was a considerable diminution in the speed of the reaction towards the end, when the formation of the final compound was almost complete. Apparently the formation of the two compounds proceeds simultaneously, or the compound $MICl_4$ is formed without the intermediate formation of $MICl_2$; in this connexion, it may be remembered that Wells and Wheeler (*loc. cit.*) considered that the compound $RbICl_4$ decomposes at the ordinary temperature by the loss of iodine trichloride in one step, whilst at higher temperatures it loses first chlorine and then iodine monochloride; this is supported by the fact that when potassium tetrachloroiodide and mercury are placed in the same desiccator, mercuric iodide is formed. Again, it was expected that the stability of the various compounds would be indicated by the rate at which they were formed, but the reverse was the case; for example, in one experiment the first three tubes contained the iodides of cæsium, rubidium, and potassium, respectively; this is also the order of stability of the chloroiodides; after two days it was found that 1·27 grams of cæsium iodide had gained 0·10 gram, 0·65 gram of rubidium iodide had gained 0·40 gram, 1·67 grams of potassium iodide had gained 0·23 gram.

Several factors appear to affect the rate of formation besides the stability of the product; one of the most important is the degree of dryness of the solid iodide; an immediate increase in the rate of change follows the introduction of a trace of water, whilst lithium iodide, containing three molecules of water of crystallisation, always reacts rapidly. Rapid reactions are also obtained by using finely powdered solid in thin layers; with thick layers or crystals, the reaction takes place quickly at the surface, but only slowly throughout the mass.

The best quantitative results are obtained by using a slow stream of chlorine and a small quantity of solid; with larger quantities,

the initial displacement of the iodine in the iodide by chlorine proceeds rapidly, with the evolution of much heat (greatest in the case of lithium iodide and least with cæsium iodide), so that the liberated iodine is partly vaporised and is lost; at a slower rate, the temperature does not appreciably rise; with iodides such as those of rubidium and cæsium, the iodine at first set free appears to combine with the unchanged iodide to form the tri-iodides, which have a low vapour pressure. All the compounds obtained by this method are yellow powders; the colour shows a marked gradation with the atomic weight of the metal, the cæsium compound being a mustard-yellow, whilst that formed from lithium iodide is a fine deep orange.

Lithium Iodide.—The anhydrous compound has not been obtained in a pure state; the compound $LiI,3H_2O$ was therefore prepared, and the crystals, dried on filter-paper, were used, since the substance is too deliquescent to powder. At the same time, another part of the specimen was analysed. (Found: I = 68·7. Calc., I = 67·5 per cent.)

0·8526 Gram of the crystals gained 0·6549 gram of chlorine, a gain of 76·8 per cent., whilst the theoretical gain is 76·7 per cent. for the formation of $LiICl_4,xH_2O$ from LiI,xH_2O, containing 68·7 per cent. of iodine. On analysis by titration with arsenite solution, the amount of chlorine gained by the lithium iodide was found to be 71·8 per cent., and with a second preparation, 71·7 per cent.

When the chlorine first comes in contact with the lithium iodide, the latter becomes deep reddish-brown and moist on the surface; the crystals then melt and much heat is evolved, but there are no copious fumes of iodine chloride as there are in the case of iodine itself; liquid drops do appear on the sides, but these are only faintly coloured and are probably drops of moisture vaporised by the heat of the reaction. Finally, the whole is converted into an orange-coloured solid. The melting is due to the fact that the lithium iodide contains enough water to dissolve the lithium chloride which is formed at first, whilst both lithium iodide and the chloroiodide melt below 80°. The final compound is a solid at the ordinary temperature. Wells and Wheeler have shown that the crystals obtained from solution have the formula $LiICl_4,4H_2O$, whilst in the present case there is only enough water to give the compound $LiICl_4,3H_2O$. The reaction was complete in two days.

Ammonium Iodide.—The salt was recrystallised from water, and was then heated in an air-oven at 150° for some time, and was kept in the desiccator until required. Chlorine quickly changed it to bluish-black by displacing the iodine, and then the yellow

colour of the iodochloride appeared. The weight became constant in two or three days. 1·1512 Grams of ammonium iodide gained 1·1151 grams of chlorine, corresponding with 96·86 per cent., whilst the formation of NH_4ICl_4 requires a gain of 97·85 per cent. A determination of the extra halogen by the arsenite method gave a result corresponding with a gain of 95·94 per cent., a second preparation giving 94·99 per cent.

Sodium Iodide.—The salt was recrystallised from water in a desiccator over sulphuric acid. The crystals so obtained were powdered and replaced in the desiccator until used. The reaction followed a similar course to that with ammonium iodide, but a longer time was required to reach constant weight. In two experiments, 0·7587 gram gained 0·6927 gram, or 91·3 per cent., and 0·7956 gram gained 0·7439 gram, corresponding with 93·50 per cent; $NaICl_4$ requires a gain of 94·61 per cent. A specimen analysed by sodium arsenite gave 92·77 per cent.

Potassium Iodide.—The salt was recrystallised from water, dried, and powdered. Results similar to those with the previous two compounds were obtained, but in some cases a long time was required to reach constancy of weight. 1·0727 Grams of potassium iodide gained 0·9111 gram, equivalent to 84·94 per cent.; analysis by sodium arsenite gave extra halogen equivalent to a gain of 82·31 per cent., whilst the formation of $KICl_4$ requires 85·44 per cent.

Rubidium Iodide.—The salt was prepared by repeated evaporation of the chloride with hydriodic acid, and was then recrystallised from water. On coming in contact with chlorine, it first turned bluish-black and then yellow; in one experiment, the formation of the yellow compound did not commence simultaneously over the whole surface, but at a number of points, which appeared to act as nuclei, giving a very striking appearance of a number of bright yellow spots on a bluish-black background. 0·6545 Gram gained 0·4366 gram of chlorine, corresponding with 66·7 per cent., whilst $RbICl_4$ requires a gain of 66·8 per cent. Since very little of the rubidium salt was available, it was not analysed by sodium arsenite, but was heated until it was white. 1·0911 Grams of the chloroiodide lost 0·7234 gram of iodine trichloride, a loss of 66·3 per cent. In the conversion of the chloroiodide, $RbICl_4$, to rubidium chloride, the loss should be 65·9 per cent. The formation of the compound proceeded rapidly, and was complete in from three to six days.

Cæsium Iodide.—This salt was prepared in the same way as the rubidium compound; the first specimen made reacted very slowly; even the first stages, where the cæsium iodide was being converted

into the chloride, were slow, enabling the change of colour from white, through pale brown, brown, chocolate, to bluish-black to be followed. The pale brown colour observed at the start is possibly due to the formation of polyiodides, the first traces of iodine set free at once uniting with the unchanged cæsium iodide, so that the colour of free iodine is not observed until a later stage; the same colour is produced when solid cæsium iodide and iodine are shaken together. Compounds such as ammonium tri-iodide are much less stable than cæsium tri-iodide, which may account for the fact that the colour of iodine appears as soon as the chlorine comes into contact with ammonium iodide.

A more rapid reaction was obtained in an experiment using a small quantity of finely divided cæsium iodide, obtained by preparing the tri-iodide by crystallisation from solution and by heating this at 180° until it was quite white. 0·1986 Gram of cæsium iodide gained 0·1087 gram of chlorine in six days; the increase in weight corresponds with 54·7 per cent., which is the theoretical gain for the formation of $CsICl_4$. 0·3073 Gram of $CsICl_4$ lost 0·1794 gram on heating, corresponding with 58·3 per cent.; the theoretical loss is 58·1 per cent.

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[*Received, April 15th*, 1918.]

LXXX.—*Hydroxylamine Platinum Bases.*

By LEO ALEXANDROWITSCH TSCHUGAEV and ILJA ILJITSCH TSCHERNJAEV.

COMPOUNDS containing hydroxylamine and platinum were discovered by Lossen (*Annalen*, 1871, **160**, 242), and were studied in more detail by Alexander (*ibid.*, 1893, **246**, 239), and later by Ulenhuth (*ibid.*, 1900, **311**, 120).

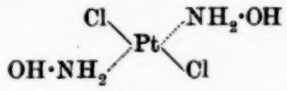
Hydroxylamine, like ammonia, combines with salts of bivalent platinum to form a series of complex compounds which are fairly closely analogous to the well-known ammoniacal platinum bases and to the corresponding derivatives of organic amines, sulphides, etc.

Free hydroxylamine and potassium platinochloride interact with the formation of tetrahydroxylaminoplatinous chloride,

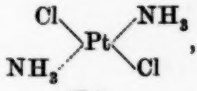
$$[Pt4NH_2{\cdot}OH]Cl_2,$$

an analogue of the salts of Reiset's Base I, $[Pt4NH_3]X_2$, and, like

these, this chloride is precipitated by potassium platinochloride to form the compound, $[Pt4NH_2{\cdot}OH]PtCl_4$, analogous to Magnus's green salt. Further, the chloride is decomposed by heating with hydrochloric acid, with the production of *trans*-dichlorodihydroxylaminoplatinum (*A*),



(*A.*)



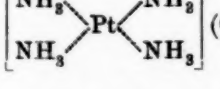
(*B.*)

which is similar, in its mode of formation and properties (see appendix), to the chloride of Reiset's Base II (*B*).

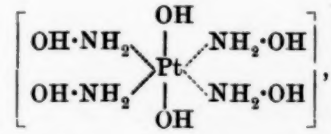
The study of these compounds has shown that hydroxylamine plays the same rôle in the molecule as does ammonia in ammoniacal platinum bases, this conclusion being confirmed by the existence of a mixed base, $[Pt2NH_3,2NH_2{\cdot}OH]X_2$, which may be regarded as Reiset's Base I with ammonia partly substituted by hydroxylamine. Some derivatives of this base are described, although very incompletely, by Alexander (*loc. cit.*).

In spite of the very close similarity between the hydroxylamine-platinum bases and the corresponding compounds containing ammonia in place of hydroxylamine, there is a marked difference in their chemical behaviour, as well as in their mode of formation. For example, hydroxylamine is more readily eliminated from the complex platinum compounds than ammonia; it was also not possible to obtain the *cis*-modification of dihydroxylaminoplatinous chloride, $[Pt2NH_2{\cdot}OH,Cl_2]$, in the usual way, namely, by the interaction of free hydroxylamine and potassium platinochloride, although the corresponding derivatives of ammonia and of organic amines are readily formed by a similar method.

Perhaps the most interesting fact to be noticed in this connexion is that by complete substitution of hydroxylamine for ammonia the very readily soluble compound $Pt4NH_3(OH)_2$, possessing strong basic properties and analogous to the alkali hydroxides, is transformed into the comparatively weak base $Pt4NH_2{\cdot}OH,(OH)_2$, almost insoluble in water and more similar to magnesia. For this reason, it was suggested by Werner ("Neuere Anschauungen auf dem Gebiete der anorganischen Chemie," 3rd ed., 5, 197) that a different constitution,



and

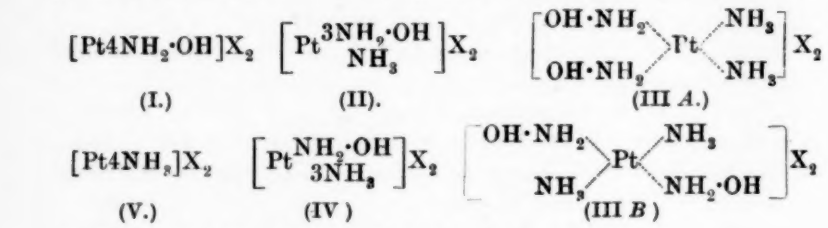


must be attributed to these two bases, the co-ordination numbers

being 4 in the case of Reiset's Base I and 6 in the corresponding hydroxylamine compound.

In view of the great interest attaching to these remarkable facts and relations, we decided to undertake a systematical investigation of the hydroxylamine-platinum bases, and particularly of the mixed bases containing hydroxylamine and ammonia (or amines), in order to elucidate the influence of the progressive substitution of hydroxylamine for ammonia.

Of the six compounds theoretically possible and correspon ling with the general formula $[Pt(NH_2{\cdot}OH)_n(NH_3)_{4-n}]X_2$, only three



(I.) (II). (III *A*.)

(V.) (IV) (III *B*)

(I, III*B*, and V) have been previously described.

We have succeeded in preparing all the missing members of the series, and have established their constitution and their relation to other hydroxylamino-ammoniacal platinum bases, so far as it was possible in the present state of our knowledge of the chemical constitution of these complex compounds.

Considering first the two isomeric compounds corresponding with the formulæ III*A* and III*B*, the chloride of the former, namely, *cis-diamminodihydroxylaminoplatinous chloride* (III*A*, where X = Cl) may be prepared by the action of free hydroxylamine on *cis*-dichlorodiamminoplatinum (Peyrone's chloride).

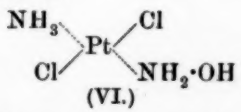
It contains the bivalent, colourless, complex cation

$$[Pt2NH_3,2NH_2{\cdot}OH]^{\cdot\cdot},$$

and gives a very characteristic platinochloride,

$$[Pt2NH_3,2NH_2{\cdot}OH]PtCl_4,$$

which forms rose-violet, microscopical needles. The constitution of the salts of this series is proved by their mode of formation, by the ionic character of the two electronegative radicles, and by the decomposition of the chloride with hydrochloric acid. In this reaction, the mixed chloride,

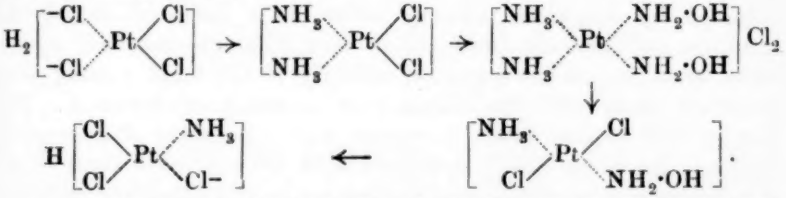


(VI.)

is formed in the first stage, and by continued action of the acid the second molecule of hydroxylamine is eliminated, Cossa's acid,

$[PtNH_3Cl_3]H$, and finally chloroplatinous acid, $H_2[PtCl_4]$, being obtained.

In view of the fact that Peyrone's chloride, the starting point in the preparation of the chloride III*A*, is prepared from chloroplatinous acid and ammonia, it will be seen that the synthesis of the salt III*A* and its degradation form a cycle, as represented by the following scheme:



In the same way, the isomeric salt III*B* may be obtained from the chloride of Reiset's Base II (*B*, p. 885), or by the action of liquid anhydrous ammonia on *trans*-dichlorodihydroxylaminoplatinum (*A*, p. 885).

Possibly the same chloride, in a slightly impure state, was prepared by Alexander by the interaction of *trans*-dichlorodihydroxylaminoplatinum and aqueous ammonia.

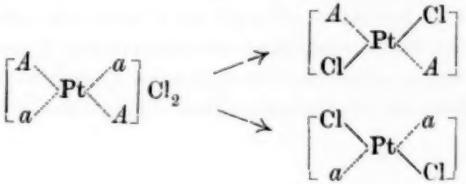
The existence of the bivalent complex cation,

$$[Pt2NH_3,2NH_2{\cdot}OH]^{\cdot\cdot},$$

in an aqueous solution of the chloride III*B* may be proved by various reactions; for example, potassium platinochloride gives a green platinochloride, $[Pt2NH_3,2NH_2{\cdot}OH]PtCl_4$, sparingly soluble in water, and potassium palladochloride and other salts of complex acids act similarly. The chlorine atoms of the chloride III*B* are both ionised in aqueous solution. From these facts, and especially from the mode of formation of this salt, its constitution as *trans-diamminodihydroxylaminoplatinous chloride* (III*B*, where X = Cl) may be regarded as sufficiently established.

The result of the action of hydrochloric acid on this substance is also in accordance with this conclusion, *trans*-dichlorodiamminoplatinum (*B*, p. 885) being the only product.

According to Jörgensen, the degradation of mixed complex bases corresponding with the *trans*-configuration gives normally two different products, both of which are *trans*-derivatives, thus:



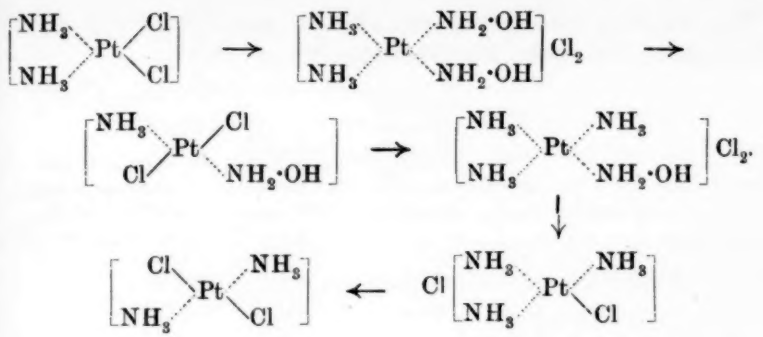
The degradation of the chloride III*B* proceeds, therefore, quite normally in so far as it gives rise to a *trans*-dichloro-derivative with two identical groups *A*, and the constitution assumed above for this chloride is especially confirmed by the fact that it gives the chloride of Reiset's Base II.

As regards the formation of only one product in this reaction instead of two, it may be remarked that the two compounds obtained by Jörgensen and by others in a series of analogous instances are generally produced in very different relative proportions, according to the degree of stability of the bond uniting the platinum atom with the molecule of ammonia or amine *A*. In fact, as will be seen later, it appears that a molecule of hydroxylamine is far more loosely combined with the platinum atom than is a molecule of ammonia, and apparently to this difference may be due the discrepancy between Jörgensen's rule and the course of degradation of the chloride III*B*.

Dichloroamminohydroxylaminoplatinum (VI, p. 886) is a very suitable starting point for the preparation of the two remaining members of our series of mixed ammonia-hydroxylaminoplatinum bases, namely, *amminotrihydroxylaminoplatinous chloride* (II, where X=Cl) and *triamminohydroxylaminoplatinous chloride* (IV, where X=Cl).

The chloride, IV, is best prepared by the interaction of dichloroamminohydroxylaminoplatinum (VI) and liquid ammonia in a sealed tube. Its constitution may be deduced from this mode of formation and from its chemical behaviour. The two chlorine atoms are immediately ionised in aqueous solution, and the complex radicle, $[Pt_3NH_3,NH_2{\cdot}OH]^{\cdot\cdot}$, has the properties of a bivalent cation. By treatment with potassium platinochloride, a green compound, $[Pt3NH_3,NH_2{\cdot}OH]PtCl_4$, analogous to the well-known Magnus's salt, is precipitated.

The most interesting results were obtained by the action of hydrochloric acid on the chloride (IV). The main product of this reaction is Cleve's chloride, $[Pt3NH_3Cl]Cl$, the molecule of hydroxylamine being displaced by a chlorine atom. This result not only proves the existence of the group $Pt3NH_3$ in the chloride, IV, but also affords a direct confirmation of the weakness of the bond $Pt...NH_2{\cdot}OH$ in comparison with the bond $Pt...NH_3$. A more energetic action of hydrochloric acid on Cleve's chloride results, as is well known, in the formation of the chloride of Reiset's Base II. Thus it is possible to effect the conversion of Peyrone's chloride into the isomeric chloride of Reiset's Base II by the following consecutive stages:



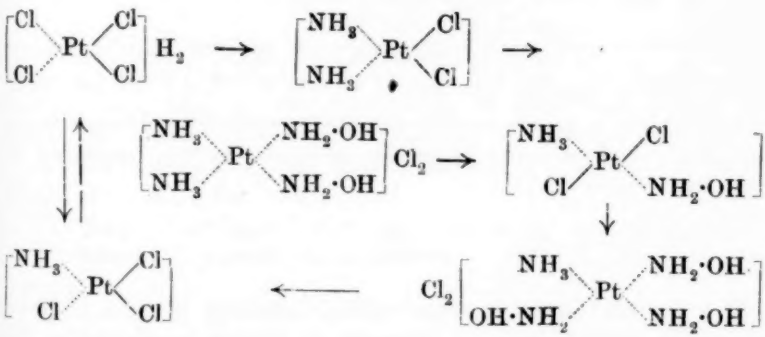
Amminotrihydroxylaminoplatinous chloride (II) is readily obtained from the chloride VI by the action of free hydroxylamine in aqueous solution. The constitution of this chloride follows from its mode of formation, from the inorganic character of the two chlorine atoms, and of the complex radicle, $PtNH_3,3NH_2{\cdot}OH$, which forms a bivalent cation (the platinochloride,

$$[PtNH_3,3NH_2{\cdot}OH]PtCl_4,$$

was obtained in rose-violet crystals), and especially from the study of its degradation products. By the action of hydrochloric acid, it gives Cossa's acid, $[PtNH_3{\cdot}Cl_3]H$, which then by further action of the acid furnishes chloroplatinous acid.

The relative weakness of the bond $Pt...NH_2{\cdot}OH$ is again demonstrated by this reaction.

It will be observed that the formation and degradation of the chloride, II, may also be represented by a cycle:



In addition to the above experiments, the behaviour of the *trans*-chloride, $[Pt2NH_2{\cdot}OH,Cl_2]$, towards pyridine was studied and found to be in perfect accordance with its behaviour towards ammonia.

The following table gives some physical properties of the mixed chlorides of the series $[Pt(NH_2{\cdot}OH)_n(NH_3)_{4-n}]Cl_2$:—

Compound.	Solubility. (Grams in 100 grams of 71·4 per cent. alcohol.)	Molecular conductivity at 25° V = 1000 litres.	Colour of the corresponding platinichloride.
$[Pt4NH_3]Cl_2$	—	261·0	Green (Magnus's salt)
$[Pt3NH_3,NH_2{\cdot}OH]Cl_3$	1·36	—	Green
$[Pt2NH_3,2NH_2{\cdot}OH]Cl_2$ (*trans*)	0·136	251·0	Dark green
$[Pt2NH_3,2NH_2{\cdot}OH]Cl_2$ (*cis*)	0·22	246·0	Reddish-violet
$[PtNH_3,3NH_2{\cdot}OH]Cl_2$	0·96	200·0	Rose-violet
$[Pt4NH_2{\cdot}OH]Cl_2$	0·28	—	Lilac

Experimental.

cis-*Diamminodihydroxylaminoplatinous Chloride* (III*A*, where X = Cl).

A mixture of 1 gram of Peyrone's chloride, 0·6 gram of hydroxylammonium chloride, 3·5 c.c. of 10 per cent. sodium hydroxide solution, and 7 c.c. of water was gently heated with frequent shaking until complete solution occurred. On cooling, the chloride separated in colourless needles or prisms, which were recrystallised from dilute hydrochloric acid and dried in the air:

0·1256 gave 0·0666 Pt. Pt = 53·01.
0·2333 ,, 0·1855 AgCl. Cl = 19·67.
0·1832 ,, 21·5 c.c. N_2 (moist) at 20·2° and 776 mm. N = 15·32.

$PtH_{12}O_2N_4Cl_2$ requires Pt = 53·27; Cl = 19·37; N = 15·30 per cent.

The substance is very readily soluble in water, the chlorine being completely ionised. The molecular conductivity was measured in aqueous solution at 25°:

V	125	250	500	1000
μ	226	232	239·5	276

The *platinochloride* separated from a solution of 0·65 gram of the above chloride in 5 c.c. of water on adding a solution of 0·8 gram of potassium platinochloride in 5 c.c. of water. It forms reddish-violet needles, and may be recrystallised from warm water. It is much more readily soluble than the green Magnus's salt.

The insoluble Magnus's salt is precipitated from its aqueous solution on the addition of Reiset's Base I,

$[Pt2NH_3,2NH_2{\cdot}OH]PtCl_4 + [Pt4NH_3]Cl_2 =$
$[Pt4NH_3]PtCl_4 + [Pt2NH_3,2NH_2{\cdot}OH]Cl_2$:

0·1119 gave 0·0675 Pt. Pt = 60·14.

$Pt_2H_{12}O_2N_4Cl_4$ requires Pt = 60·22 per cent.

The *palladochloride* was obtained from the chloride (III*A*) and potassium palladochloride. It separates as a dirty, green, microcrystalline powder sparingly soluble in water:

0·1053 gave 0·1107 AgCl. Cl = 26·06.

$PtPdH_{12}O_2N_4Cl_4$ requires Cl = 26·08 per cent.

trans-*Diaminodihydroxylaminoplatinous Chloride* (III*B*, where X = Cl).

This salt was prepared in the same manner as the *cis*-isomeride from the chloride of Reiset's Base II. It crystallises from hot water, in which it is readily soluble, in colourless prisms, and is precipitated from aqueous solutions by hydrochloric acid or alcohol:

0·1549 gave 0·0825 Pt. Pt = 53·24.
0·0944 ,, 0·0727 AgCl. Cl = 19·13.
0·1930 ,, 25·3 c.c. N_2 at 21° and 773 mm. N = 15·12.

$PtH_{12}O_2N_4Cl_2$ requires Pt = 53·27; Cl = 19·37; N = 15·30 per cent.

The chlorine atoms are both completely ionised, and are precipitated by silver nitrate. The following numbers were obtained for the molecular conductivity in aqueous solution at 25°:

V	250	500	1000
μ	229	240	251

The aqueous solution is neutral towards litmus, indicating the absence of appreciable hydrolysis. By heating the chloride with hydrochloric acid on the water-bath, as mentioned above, two molecular proportions of hydroxylamine are eliminated with the formation of the chloride of Reiset's Base II. (Found: Pt = 65·11. Calc.: Pt = 65·11 per cent.)

The *trans*-chloride may also be obtained by the interaction of *trans*-dichlorodihydroxylaminoplatinum, $[Pt2NH_2{\cdot}OH,Cl_2]$, and ammonia.

This reaction was first studied by Alexander (*loc. cit.*), who employed four molecular proportions of ammonia and one of the chloro-compound in aqueous solution, and obtained a flocculent, reddish-white precipitate, which he regarded as the free base, $[Pt2NH_2{\cdot}OH,2NH_3](OH)_2$. By dissolving it in cold dilute hydrochloric acid, he states that the chloride, $[Pt2NH_2{\cdot}OH,2NH_3]Cl_2$, was obtained, yielding a dark green platinochloride.

Alexander stated, further, that his chloride was precipitated by alkali hydroxides, yielding an amorphous, gelatinous mass insoluble in water. On the other hand, his chloride was very unstable towards concentrated hydrochloric acid, which decomposed it with the loss of two molecular proportions of ammonia and the formation of *trans*-dichlorodihydroxylaminoplatinum.

The properties of this substance being thus entirely different from the properties of the chloride described above, we decided to repeat the corresponding part of Alexander's work. It appeared from our experiments that, under the conditions mentioned by this author, ammonia indeed gives with the compound

$$[Pt2NH_2{\cdot}OH,Cl_2]$$

an insoluble, amorphous, pale yellow precipitate, but this is by no means formed by the addition of ammonia to dichlorodihydroxylaminoplatinum. On the contrary, its composition corresponds approximately with the formula $[PtNH_2{\cdot}OH,Cl(OH)]$ of a hydroxo-compound, one atom of chlorine being displaced by a hydroxyl group, and, as was to be expected, we were unable to obtain from this substance the mixed chloride,

$$[Pt2NH_3,2NH_2{\cdot}OH]Cl_2,$$

by the action of hydrochloric acid.

The addition of ammonia to the compound $[Pt2NH_2{\cdot}OH,Cl_2]$, may be easily effected by using anhydrous liquid ammonia and by operating in a sealed tube. An orange solution is obtained at first, which is gradually decolorised. At the same time, a colourless, crystalline precipitate of the chloride,

$$[Pt2NH_3,2NH_2{\cdot}OH]Cl_2,$$

separates. The composition of the substance was verified by analysis, and its identity with the *trans*-isomeride was proved by its characteristic reactions. It was specially ascertained that this chloride yielded, on heating with with hydrochloric acid, the chloride of Reiset's Base II. *trans*-Dichlorodihydroxylaminoplatinum could not be obtained under these conditions.

The *platinochloride* of the salt just described may be obtained by the addition of potassium platinochloride to its solution; it forms microscopic, dark green needles, which are sparingly soluble in cold water and may be recrystallised from hot water containing a little hydrochloric acid. It is much more stable than the *cis*-isomeride:

0·0714 gave 0·0438 Pt. Pt = 61·40.

0·1335 „ 10·5 c.c. N_2 (moist) at 21° and 773 mm. N = 9·07.

$Pt_2H_{12}O_2N_4Cl_4$ requires Pt = 61·75; N = 8·86 per cent.

The *palladochloride*, similarly prepared by the aid of ammonium palladochloride, forms microscopic, olive-green needles:

0·0665 gave 0·0698 AgCl. Cl = 26·00.

$PtPdH_{12}O_2N_4Cl_4$ requires Cl = 26·08 per cent.

trans-*Dichloroamminohydroxylaminoplatinum* (VI, p. 886).

One gram of the *cis*-chloride, $[Pt2NH_3,2NH_2{\cdot}OH]Cl_2$, is heated on the water-bath for one and a-half hours with 5 c.c. of hydrochloric acid (D 1·19) and 20 c.c. of water. The colour of the solution must remain yellow; if it turns orange-red, the reaction has proceeded too far. On cooling, the mixed compound separates in characteristic aggregates of dentate yellow crystals, which may be recrystallised from very dilute hydrochloric acid. The yield is 70—90 per cent. of the theoretical:

0·0934 gave 0·0576 Pt. Pt = 61·64.

0·1578 „ 12·4 c.c. N_2 (moist) at 20° and 756 mm. N = 8·91.

0·1119 „ 0·1004 AgCl. Cl = 22·19.

$PtH_6ON_2Cl_2$ requires Pt = 61·75; N = 8·76; Cl = 22·43 per cent.

The substance is sparingly soluble in cold, but much more readily so in hot water, and very sparingly so in alcohol.

The aqueous solution is greenish-yellow, and immediately after the addition of silver nitrate gives only a slight opalescence, the precipitation of silver chloride occurring only gradually and being accelerated by heating.

It must accordingly be assumed that the chlorine atoms are in direct union with the platinum. This conclusion was confirmed by the determination of the molecular conductivity (in aqueous solution at 25°), which gave very low values almost approaching zero: $\mu = 2{\cdot}05$ (V = 526). The values of μ rise very quickly with time, hydrolysis evidently taking place under these conditions.

By the prolonged action of hot hydrochloric acid, the substance is decomposed with the elimination of one molecular proportion of hydroxylamine and formation of the complex acid, $[PtNH_3,Cl_3]H$, discovered by Cossa:

$$[PtNH_3,NH_2{\cdot}OH,Cl_2] + 2HCl = (PtNH_3,Cl_3)H + NH_2{\cdot}OH,HCl.$$

This acid was identified by precipitating the solution with the chloride of Reiset's Base I. The characteristic orange-yellow quadratic scales of Cossa's salt, $[PtNH_3,Cl_3]_2[Pt4NH_3]$, were obtained, and its composition was verified by analysis. (Found: Pt = 64·92. Calc.: Pt = 65·10 per cent.)

Triamminohydroxylaminoplatinous Chloride, $[Pt(NH_3)_3,NH_2{\cdot}OH]Cl_2$.

This substance was prepared by the interaction of the mixed salt just described and anhydrous liquid ammonia in a sealed tube at the ordinary temperature. After the expulsion of free ammonia, a colourless, crystalline powder remained which crystallised from 80 per cent. alcohol in colourless, glistening plates very readily soluble in water:

0·1206 gave 0·0673 Pt. Pt = 55·83.
0·0950 ,, 0·0781 AgCl. Cl = 20·34.
0·1436 ,, 20·1 c.c. N_2 (moist) at 21° and 770 mm. N = 16·07.
$PtH_{12}ON_4Cl_2$ requires Pt = 55·73; Cl = 20·25; N = 16·00 per cent.

On heating with hydrochloric acid, the substance is decomposed, hydroxylamine being eliminated and Cleve's salt, $[Pt3NH_3,Cl]Cl_2$, being formed, which was detected by means of its very characteristic platinochloride, $[Pt3NH_3,Cl]_2PtCl_4$.

The *platinochloride*, $[Pt3NH_3,NH_2{\cdot}OH]PtCl_4$, was obtained by precipitating the preceding chloride with potassium platinochloride, as a pale green powder consisting of microscopic needles which may be recrystallised from hot water:

0·1001 gave 0·0634 Pt. Pt = 63·34.
0·2186 ,, 17·4 c.c. N_2 (moist) at 21° and 773 mm. N = 9·17.
0·1103 ,, 0·1038 AgCl. Cl = 23·28.
$Pt_2H_{12}ON_4Cl_4$ requires Pt = 63·34; N = 9·10; Cl = 23·01 per cent.

By heating this platinochloride with hydrochloric acid, hydroxylamine is eliminated, and the characteristic pink plates of Cleve's salt, $[Pt3NH_3Cl]_2PtCl_4$, separate, especally on cooling, together with unchanged substance. The separation of the two can be effected by levigation and by subsequent recrystallisation from very dilute hydrochloric acid.

Amminotrihydroxylaminoplatinous Chloride, $[PtNH_3,(NH_2{\cdot}OH)_3]Cl_2$.

The mixed chloride, $[PtNH_3,NH_2{\cdot}OH,Cl_2]$, was gently heated with the theoretical quantity of hydroxylamine hydrochloride and the equivalent quantity of sodium hydroxide in aqueous solution. The new chloride is very readily soluble in water, and may be separated from a concentrated aqueous solution by the addition of alcohol or of hydrochloric acid. It forms transparent, colourless crystals;

0·1061 gave 0·0542 Pt. Pt = 51·03.

0·1126 „ 14·4 c.c. N_2 (moist) at 19·4° and 765·5 mm. N = 14·68.

0·1058 gave 0·0788 AgCl. Cl = 18·42.

$PtH_{12}O_3N_4Cl_2$ requires Pt = 51·07; N = 14·67; Cl = 18·55 per cent.

The chlorine atoms are both completely ionised. The figures obtained for the molecular conductivity at 25° are: V = 1000; μ = 240.

The *platinochloride*, precipitated from a solution of the preceding salt by means of potassium platinochloride, forms microscopic, rose-violet needles:

0·1119 gave 0·0675 Pt. Pt = 60·14.

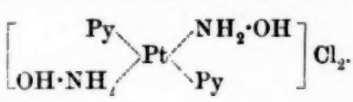
$Pt_2H_{12}O_3N_4Cl_4$ requires Pt = 60·22 per cent.

The *palladochloride*, similarly obtained from ammonium palladochloride, crystallises in reddish-violet needles:

0·0567 gave 0·0587 AgCl. Cl = 25·62.

$PtPdH_{12}O_3N_4Cl_4$ requires Cl = 25·37 per cent.

trans-*Dipyridinodihydroxylaminoplatinous Chloride*,



This substance was prepared by the interaction of pyridine and *trans*-dichlorodihydroxylaminoplatinum. Dry pyridine readily dissolves the dichloro-compound, forming an orange-yellow solution, which loses its colour very quickly, and at the same time a colourless, crystalline powder separates. The mixture is heated for some minutes and filtered after cooling. The residue is then washed with alcohol and recrystallised from hot water:

0·0986 gave 0·0392 Pt. Pt = 39·76.

0·1133 „ 0·0649 AgCl. Cl = 14·1.

$C_{10}H_{16}O_2N_4Cl_2Pt$ requires Pt = 39·80; Cl = 14·4 per cent.

Potassium platinochloride precipitates the platinochloride, $[Pt2Py,(NH_2{\cdot}OH)_2]PtCl_4$, which crystallises in microscopic, pale rose prisms:

0·1450 gave 0·0746 Pt. Pt = 51·41.

$C_{10}H_{16}O_2N_4Cl_4Pt_2$ requires Pt = 51·61 per cent.

On heating with hydrochloric acid, *trans*-dipyridinodihydroxylaminoplatinous chloride behaves in a similar manner to the corresponding ammonia compound; the substance loses two molecular proportions of hydroxylamine and dichlorodipyridinoplatinum is

formed. (Found: Pt=45·78. Calc.: Pt=46·03 per cent.) This substance possesses all the properties assigned to it by Jörgensen (*J. pr. Chem.*, 1886, [ii], **33**, 489).

Appendix.

trans-*Dichlorodihydroxylaminoplatinum* (*A*, p. 885).

This substance, as stated by Alexander, is easily obtainable from the tetrahydroxylamine compound, $[Pt4NH_2{\cdot}OH]Cl_2$, by heating it with dilute hydrochloric acid, and separates from the solution, on cooling, in large orange needles or prisms.

In complete accordance with Werner's theory, it possesses the property of a typical non-electrolyte, for it gives only a slight opalescence immediately after the addition of silver nitrate to its aqueous solution, whilst the complete precipitation of silver chloride is effected only after a long time, but very quickly by heating. The conductivity measurements gave also, as was to be expected, very low figures approaching zero: $V=287$ ($t=25°$); $\mu=1·25$.

A more thorough study of this substance showed that it has the property of forming double compounds with certain chlorides, such as the chloride of Reiset's Base I and cæsium chloride.

Two grams of the compound, $[Pt2NH_2{\cdot}OH,Cl_2]$, and 2 grams of the chloride, $[Pt4NH_3]Cl_2$, were dissolved in 6 c.c. of hot water. On cooling, the additive compound separated in well-defined, pale yellow, prismatic crystals fairly readily soluble in water, the composition of which corresponds with the formula

$$[Pt2NH_2{\cdot}OH,Cl_2],[Pt4NH_3]Cl_2,2H_2O:$$

1·4070 gave 0·0722 H_2O. $H_2O=5·13$.

0·2357 „ 0·1309 Pt. Pt=55·54.

$Pt_2H_{18}O_2N_6Cl_4,2H_2O$ requires $H_2O=5·13$; Pt=55·58 per cent.

The water is eliminated at 100—110°, but not in a vacuum desiccator over sulphuric acid (the anhydrous salt gave Pt=58·51; Calc.: Pt=58·58 per cent.).

The double compound with cæsium chloride,

$$[Pt2NH_2{\cdot}OH,Cl_2],2CsCl,$$

was obtained in a similar manner and has almost the same properties:

0·1658 gave 0·1684 Cs_2PtCl_6. Cs=40·08.

0·1854 „ 0·0544 Pt. Pt=29·34.

0·1659 „ 0·1435 AgCl. Cl=21·40.

$PtCs_2H_6O_2N_2Cl_4$ requires Cs=39·76; Pt=29·15; Cl=21·22 per cent.

The existence of these double compounds may be considered as an indication of the property possessed by the non-electrolyte,

$[Pt2NH_2{\cdot}OH,Cl_2]$, of combining with two chlorine ions to yield the unstable complex anion, $[Pt2NH_2{\cdot}OH,Cl_4]''$.

Accordingly, the constitution of the double compounds may be represented by the formulæ $[Pt2NH_2{\cdot}OH,Cl_4][Pt4NH_3]$ and $[Pt2NH_2{\cdot}OH,Cl_4]Cs_2$.

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LXXXI.—*Trimorphic Change of 4-Nitroaceto-o-toluidide.*

By FREDERICK DANIEL CHATTAWAY.

CASES of trimorphic change, although several have been observed, are sufficiently rare for a new one to be of interest. The phenomenon is well shown by 4-nitroaceto-*o*-toluidide, which on crystallisation undergoes two successive transformations before a stable state is reached.

By nitrating *o*-toluidine in the presence of excess of concentrated sulphuric acid, Nölting and Collin (*Ber.*, 1884, **17**, 269) first prepared the base, and by heating with acetic anhydride converted it into the acetyl derivative. This they describe very briefly as crystallising in yellowish-white needles melting at 150—151°.

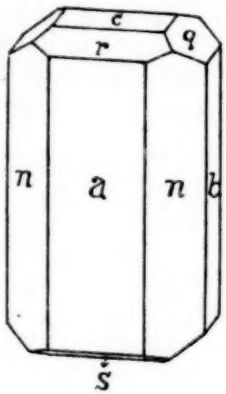
Speaking in general terms, all anilides crystallise in one of three easily recognisable forms, namely, a slender prismatic form, a compact form, and a hair-like form, and many have been obtained in two of them.

4-Nitroaceto-*o*-toluidide can be obtained in all three forms, the order of stability being: slender prismatic → compact → hair-like.

It is moderately readily soluble in boiling alcohol, giving a pale yellow solution, from which very slender prisms of the first, or α-form, separate on cooling. These are of such a pale yellow colour that when dry they appear almost colourless. If the original solution is sufficiently concentrated, they grow until the whole liquid is filled with a mass of slender crystals, generally radiating from a few points. If these crystals are allowed to remain in the mother liquor at the ordinary temperature, small, yellow, six-sided plates of the second, or β-modification, soon make their appearance, and rapidly grow at the expense of the first form, which dissolves in their neighbourhood, forming cavities occupied by one or more crystals that may increase to a considerable size

and are usually well shaped. The transformation into the second form is generally complete after the lapse of a few days if the beaker is left undisturbed, although the time taken depends greatly on the average temperature, and is much shortened by occasionally shaking the transforming mass. When the change is complete, a relatively thin layer of well-shaped, compact crystals remains at the bottom of the beaker.

After some time, often before complete transformation of the first into the second form, a third, or γ-modification, makes its appearance in tufts of colourless, hair-like crystals resembling small colonies of a mould or tiny balls of cotton wool. These increase in size, the compact form dissolving and disappearing until the whole contents of the beaker become a felted mass having a superficial resemblance to a somewhat slimy jelly. From this, the mother



liquor is removed only with difficulty by filtration or pressure. Direct transformation of the α- into the γ-form occurs if the mass of slender prismatic crystals first separating is seeded with a few crystals of the hair-like form.

All three forms, when heated, soften and melt at the same temperature, namely, 150—151°, which seems to indicate that before the fusion point is reached transformation into the form most stable near that temperature takes place.

Mr. T. V. Barker, who has very kindly examined the crystals, reports on them as follows.

The first, or α-modification, crystallises in doubly refracting needles with straight extinction.

The well-developed crystals of the β-modification belong to the monoclinic system. Forms: $a(100)$, $c(001)$, $n(210)$, $b(010)$, $q(011)$, and $r(101)$; also, occasionally, $s(\bar{1}01)$, and, very rarely, $x(021)$ and

y(012). The general habit and common forms of the crystals are shown in the figure. Crystallographic constants: 57°26′, a(48°34′)m(41°26′)b, 49°43′, 74°10′, or, alternatively, $a:b:c=1{\cdot}178:1:0{\cdot}6388$, $\beta=105°50'$. Three crystals were measured on the two-circle goniometer; following are the mean values of the most trustworthy results:

	b (010).	a (100).	n (210).	c (001)
Azimuth	Face of	0° 0′	0° 0′	*74° 10′
Polar distance ...	reference	90 0	*60 28	90 0

	q (011).	r (101).	
Azimuth	74° 10′	50° 13′	(calc. = 49° 43′)
Polar distance ...	*58 25½	90 0	

Optically, biaxial; axial plane, b(010); extinction on b(010), 37° with prism edge in the obtuse angle β. Complex-symbol: $4h\,;+16/42/+3\frac{1}{2}$.

The third, or γ-modification, crystallises in hair-like, doubly refracting needles with an extinction of 35°.

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[*Received, October 21st,* 1918.]

LXXXII.—*The Preparation of Ethylamine and of Diethylamine.*

By EMIL ALPHONSE WERNER.

IN the preparation of ethylamine and of diethylamine by the interaction of ethyl bromide and ammonia, it has been the usual practice, so far as hitherto recorded, to submit the whole of the alkyl haloid to the action of ammonia in a single operation.

This is a faulty procedure, since it conduces largely to the formation of the less useful triethylamine, with consequent loss in the yields of the primary and secondary bases. Whether the change is promoted by heat or is allowed to proceed at the ordinary temperature, the tertiary amine has been present in largest amount in the final product (compare Garner and Tyrer, T., 1916, **109**, 174).

The author has found that when ethylamine is added to an alcoholic solution of diethylammonium chloride, the displacement of the secondary amine by the primary is quantitative; thus

diethylamine only was obtained on distillation of the mixture after it had remained for an hour, whilst under similar conditions the displacement of triethylamine from its hydrochloride by diethylamine was likewise quantitative (Expts. I, II).

A fair separation of all three amines, in the same order, has been effected by fractional treatment of a solution of their salts with sodium hydroxide; the tertiary amine was first liberated, the secondary next, and the primary amine last (Expt. III).

It must be admitted that these results go to show, contrary to the commonly accepted view, that triethylamine is the weakest base of the three amines.

Reasoning on this basis, and bearing in mind the relative tendency to dissociation * of the respective 'amine' salts, a procedure has been adopted whereby the formation of triethylamine has been almost completely suppressed. Thus, from the product of two experiments, in which 2090 grams of ethyl bromide were used, only 27 grams of triethylamine were obtained, whilst the yield of ethylamine was 33·8 per cent. and of diethylamine 57·5 per cent. of the theoretical.

The influence of the proportion of ammonia to ethyl bromide on the yield of ethylamine is shown by the following results:

Molecular ratio $EtBr : NH_3$	1 : 1	1 : 4	1 : 6	1 : 8	1 : 16
Percentage yield of NH_2Et on theoretical	11·3	24·4	26·7	28·1	34·2

The necessity of maintaining a good excess of ammonia throughout the progress of the reaction is indicated by theory.

Experimental.

Preparation of Ethylamine and of Diethylamine.

Five litres of 90 per cent. alcohol were saturated with ammonia (compare this vol., p. 698) until 490 grams of the gas had been dissolved, 200 grams of ethyl bromide were added (ratio EtBr to NH_3 approximately 1 to 16), after which, at successive intervals of two days, fresh quantities of the alkyl haloid were added in the following amounts: 180, 170, 150, 130, 110, 100, 80, and, finally, 66 grams. Preliminary experiments had shown that with the above ratio of ammonia the whole of the ethyl bromide was decomposed after two days, hence the successive quantities were regulated

* The term as used here does not refer to ionisation or electrolytic dissociation.

so as to maintain the desired excess of ammonia throughout the progress of the change. In all, 1186 grams of ethyl bromide were used; ammonium bromide began to separate on the twelfth day, and on the sixteenth day the preparation was stopped. Test experiments on a small scale with pure alcohol had shown that when ammonium bromide separated in quantity in the early stage of the process, the formation of triethylamine was promoted when the reaction was prolonged. The reason is fairly obvious when the probable mechanism of the process is considered, hence it was found advantageous to use alcohol containing 10 per cent. of water.

The alcoholic solution, separated from ammonium bromide, was concentrated by distillation (the ammonia evolved was used to charge more alcohol) until nearly all the ammonium bromide formed had separated, 362 grams of which were recovered.

The solution of the hydrobromides of the mixed amines was distilled until the temperature reached 130°, in order to remove the last traces of alcohol. Where it was not found convenient to liberate the entire quantity of the mixed amines by the addition of aqueous sodium hydroxide to the residue, chloroform was used as a solvent for their separation.

Ethylammonium bromide is dissolved by chloroform to the extent of only 0·163 gram in 100 c.c. at 14°, whilst the same volume of chloroform dissolves 42 grams of diethylammonium bromide. By this means, 465 grams of pure ethylammonium bromide and 510 grams of diethylammonium bromide, containing slightly more than 5 per cent. of triethylammonium bromide, were obtained. After the separation of triethylamine (14 grams) by treatment with the requisite proportion of sodium hydroxide, 226 grams of diethylamine, collected at 56—57·5° and dried over potassium hydroxide, were obtained.

(a) *Displacement of Diethylamine by Ethylamine, and of* (b) *Triethylamine by Diethylamine.*

Expt. I.—(*a*) Nine grams of pure ethylamine were added to 12 grams of diethylammonium chloride dissolved in 30 c.c. of alcohol. After an hour, all free amine was removed by distillation. The hydrochloride prepared from the distillate gave Cl = 32·33, whilst $NHEt_2$,HCl requires Cl = 32·42 per cent. The displacement of the secondary amine from its salt was therefore complete.

Expt. II.—(*b*) Eight grams of pure diethylamine were added to 15 grams of triethylammonium chloride dissolved in 35 c.c. of

alcohol. The mixture was distilled as in the previous experiment. The hydrochloride prepared from the distillate gave Cl = 25·78, whilst NEt_3,HCl requires Cl = 25·81 per cent. The displacement of the tertiary amine by the secondary was therefore complete.

Separation of the Three Amines by Sodium Hydroxide.

Expt. III.—To a solution which contained 13·8 grams of triethylammonium chloride, 11 grams of diethylammonium chloride, and 9 grams of ethylammonium chloride dissolved in 60 c.c. of water, 4 grams of sodium hydroxide were added. The solution was well shaken, and after twenty hours the liberated amine was distilled off.

The hydrochloride prepared from it gave Cl = 26·04, whilst NEt_3,HCl requires Cl = 25·81 per cent. The amine was therefore almost pure triethylamine.

To the remaining solution, when cold, 4 grams of sodium hydroxide were added, and a similar treatment was applied.

The hydrochloride prepared from the liberated amine gave Cl = 34·44, which corresponds with a mixture, in round numbers, of diethylamine = 85 and ethylamine = 15 per cent. The residual solution was directly distilled after a final addition of sodium hydroxide. The hydrochloride prepared from the distillate gave Cl = 41·12; the liberated amine had, therefore, the approximate composition, ethylamine = 75 and diethylamine = 25 per cent. These results indicate that this method of procedure for the separation of the amines may prove useful on a larger scale, and the subject is under investigation in connexion with certain of the higher aliphatic amines.

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LXXXIII.—*The Determination of the Molecular Complexity of Liquid Sulphur.*

By Alex. Mitchell Kellas.

Sulphur has a greater molecular complexity in solution, and also throughout a considerable range of temperature in the gaseous condition, than any other element, and its complexity in the liquid state would therefore seem to be of special interest.

This was recognised by Ramsay and Shields, the pioneers, who, following up a generalisation of Eötvös (*Ann. Phys. Chem.*, 1886, [iii], **27**, 452), made the first series of determinations in connexion with the complexity of liquids, but they stated that no results could be obtained with sulphur, because of its great viscosity (T., 1893, **63**, 1089). After further attempts, Ramsay and Aston made a similar statement as a final conclusion (T., 1894, **65**, 167).

Several years ago, the author, in carrying out the usual lecture experiment of preparing the plastic modification of sulphur, drew the conclusion that viscosity could not be the cause of the failure to obtain definite results, as sulphur is quite mobile from its melting point at 115° up to about 160°, when an abrupt increase of viscosity occurs. This evidently gave a range of about 45° for the determination of the variation of molecular surface energy with temperature, which is larger than that generally used by Ramsay and Shields.

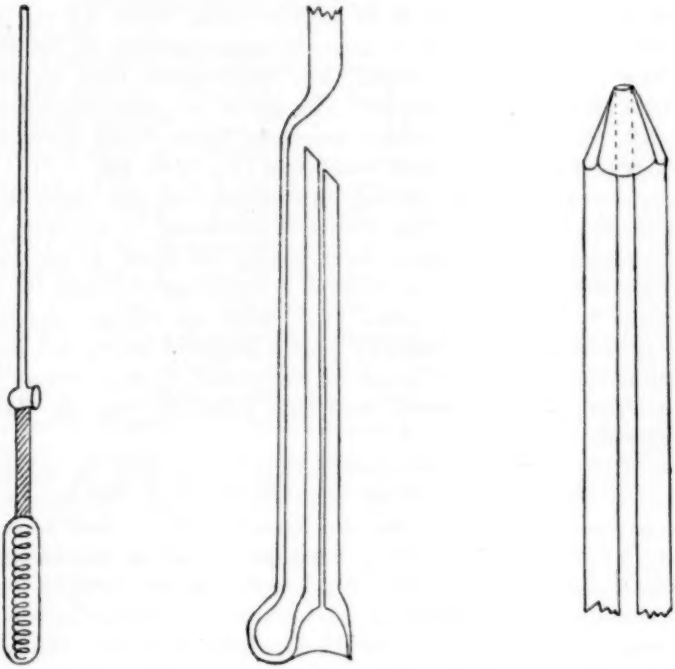
Preliminary experiments showed that it was easy to get liquid sulphur to rise from 4 to 8 cm. in capillary tubes, but also, as was to be expected from the difficulties encountered by such especially careful workers as those above mentioned, that it was impossible to obtain concordant results. As, however, great viscosity—which at this stage was regarded as an almost insuperable factor—was evidently not the cause of the discrepancies observed, the author started a series of experiments in order to determine the actual disturbing agents, and, after great difficulty, was able to devise a course of procedure which allows of the determination of the surface tension of sulphur at any temperature from its melting point to its boiling point (that is, from 115° to 445°).

Derivation of Suitable Apparatus.

It was found necessary completely to modify the apparatus employed by Ramsay and Shields, which consisted of a sealed tube partly surrounded by a vapour jacket. The capillary used by them

was attached to a small cylindrical bulb containing soft iron, which allowed of its being raised into position by means of a magnet (T., 1893, **63**, 1094). It was found possible to work satisfactorily with this apparatus only after jacketing the whole of the reaction tube, an electromagnet being employed to raise the capillary, but, as the latter frequently fractured when the sulphur solidified, thus causing great loss of time, it was eventually decided to alter the apparatus so as to allow of the use of thick-walled capillary tubes.

FIG. 1.



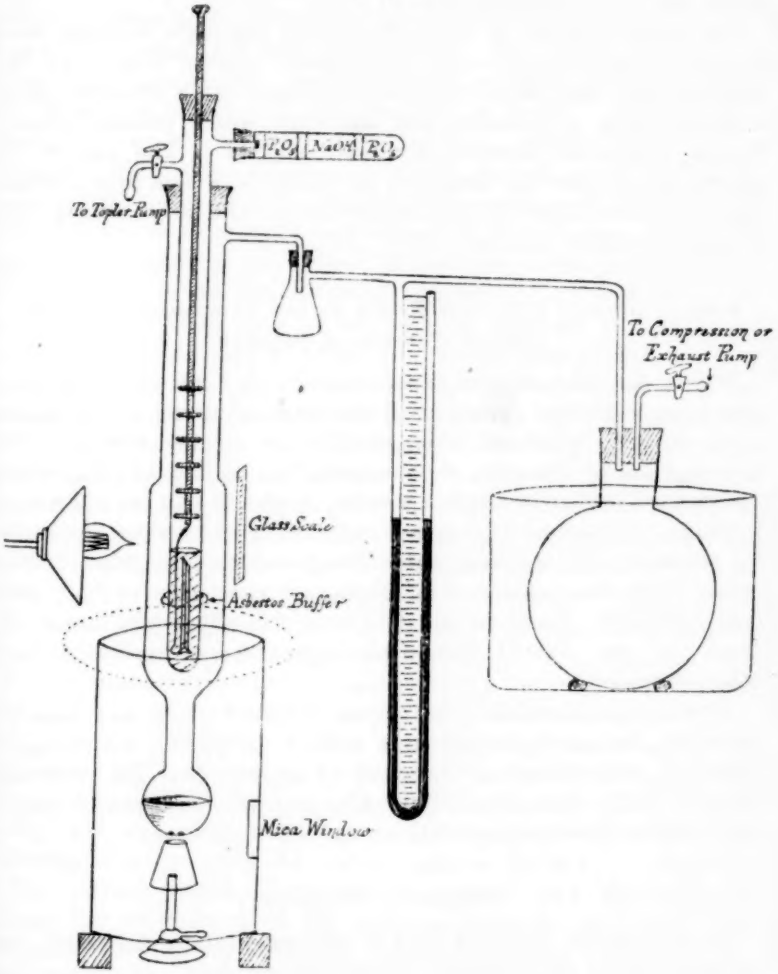
a. *b.* *c.*

After experiment, it was found that the stout-walled tubing used for making ethyl chloride jets was suitable, but, being heavy, it was necessary to manipulate it from above. The relationship between the Ramsay and Shields type of capillary and that employed in the work described below is illustrated in Fig. 1. For use in mobile sulphur, it was found convenient to bevel the top of each capillary tube at an angle of 45°, so as to prevent sulphur collecting on irregularities and trickling into the top of the tube during the course of an experiment (Fig. 1, *b*). With viscous

sulphur, however, even this precaution was insufficient, and it was eventually found necessary to bevel each capillary round the top, like a sharpened pencil (**Fig. 1**, *c*).

The capillary was contained in a long, cylindrical tube closed

FIG. 2.



by a rubber cork, through which passed a stout glass rod attached to the base of the capillary tube, as shown in **Fig. 2**. The rod was expanded into baffle-disks in its lower portion so as to prevent cooling of the surface of the sulphur by convection currents. A

side-tube provided with a tap allowed of exhaustion of the experimental tube containing the sulphur by means of a Töpler pump. The tube was surrounded by a vapour jacket, and it was eventually found preferable to use a long tube without condenser. The connexion of this jacketing tube to catch-flask, manometer, and air-chamber, which allowed of modification of the boiling point of the liquid used, is illustrated (Fig. 2).

The upper portion of the sulphur and the scale in front were strongly illuminated by an incandescent electric lamp. As the capillary and scale were necessarily a considerable distance apart, a special type of telescope was employed which focussed clearly objects within an exceptional depth of field. The gas in the experimental tube was kept dry by means of a side-tube containing phosphoric oxide and sodium hydroxide, the latter reagent also absorbing sulphur dioxide.

Factors causing Special Difficulty in the Determination of the Surface Tension of Sulphur.

During the long series of experiments carried out while a suitable apparatus was being developed, it was found that concordant results could only be obtained after purification of the sulphur. On investigation of the gases pumped off after boiling, the disturbing agents were evidently sulphur dioxide, sulphuric acid, and hydrogen sulphide, and also perhaps compounds formed from these substances by reaction with sulphur, water being an accessory factor. This agrees with the experience of Moissan (*Ann. chim. Phys.*, 1907, [viii], **10**, 433), Malus (*ibid.*, 1901, [vii], **24**, 491)—who found that fresh gas was evolved even after eighty successive fusions—and other observers.

It was found advisable not to use sulphur which had been exposed to air, as it seemed more difficult to purify, which agrees with the observations of Leonard (*Analyst*, 1901, **26**, 319) and Pollacci (*Boll. chim. farm.*, 1908, **47**, 363), who state that sulphuric acid may be present in quantities up to 0·25 per cent.

Method of Procedure.

At first it was supposed that it was desirable to start with pure sulphur, and the purest crystalline sulphur obtainable was employed. It was later found, however, that if commercial flowers of sulphur were once distilled and the middle fraction used, excellent results could be obtained after purification from sulphur dioxide and the other impurities mentioned above.

Immediately after distillation, the sulphur was poured into the

heated, dry experimental tube. The capillary tube, which had been cleaned by warming with potassium dichromate and sulphuric acid, washed with distilled water, and then heated to about 350° in a small cylindrical electric heater, was inserted in the molten sulphur and the air (or nitrogen) pumped off. The tube was then filled with dry nitrogen and the sulphur boiled for fifteen to twenty minutes; after cooling, the tube was exhausted and left to remain overnight, again filled with dry nitrogen, the sulphur boiled, and, after allowing to cool to about 140°, the capillary was raised from the liquid and the behaviour of the sulphur noted. If the sulphur were pure and the capillary tube clean, any bubbles of gas in the latter which were not spherical would be concave above and below, looking like cylinders with hemispherical ends, and between 120° and 160° would rapidly rise and escape, slight reduction of pressure invariably causing a rapid rise. If, on the contrary, the sulphur or tube were in an unsatisfactory condition, any bubble in the capillary would have more or less flattened menisci, and would not move, even on reducing pressure to a considerable extent.

If unsatisfactory, the process of boiling and exhaustion was repeated, but if the behaviour of the sulphur seemed normal, the tube was surrounded with the vapour of a liquid at a definite temperature and a series of measurements effected. Six determinations were generally carried out for temperatures below 160°, an agreement within 0·01 cm. being required, but in many cases the six readings were identical. At temperatures above 160°, on account of the enormous viscosity, 0·02 cm. was the limit of error, and fewer readings were usually taken, because of the increased length of time required for each experiment.

The substances employed as vapour jackets included glacial acetic acid (b. p. 118°), chlorobenzene (132°), bromobenzene (157°), methyl oxalate (163°), aniline (183°), ethyl benzoate (212°), quinoline (237°), bromonaphthalene (277°), diphenylamine (304°), phenanthrene (340°), and mercury (357°); boiling liquid sulphur (445°) was also used. For substances boiling above 300°, the jacketing tube was wide and had no bulb at the end.

The surface tension apparatus was filled with dry nitrogen during the purification of the sulphur, in order to prevent the formation of sulphur dioxide. Bodenstein and Caro (*Zeitsch. physikal. Chem.*, 1910, **75**, 30) have stated that sulphur oxidises slowly at 150° and rapidly near the temperature of ignition—approximately 245°—which seems to agree with the results observed. It was found to be unsatisfactory to boil the sulphur in a vacuum, as the whole mass was apt to project itself up the tube at about 200°.

Preliminary experiments seem to indicate that ammonia may be used to aid in the purification of sulphur, as might be expected from Smith and Carson's results (*Ber.*, 1902, **35**, 2992).

Determination of Radii of the Capillary Tubes Employed.

In order thoroughly to test the method of working, and also to find out whether the viscosity of sulphur affected the results in narrow tubes, seven capillaries were selected of radii varying from 0·09992 to 0·00895 cm., that is to say, from approximately 2 mm. to 0·18 mm. in diameter. The latter is smaller in bore than any of those employed by Ramsay and Shields or other workers (so far as the author has observed), water rising in it to a height of about 16 cm.

The determinations of bore were effected by means of mercury, the following being the mean values for the respective radii in cm.: (1) 0·09996, (2) 0·0721, (3) 0·05208, (4) 0·03318, (5) 0·02362, (6) 0·01523, (7) 0·00895; number (5) was afterwards found to be slightly oval in section.

Determination of the Density of Sulphur at Different Temperatures.

As trustworthy values of the density of sulphur at different temperatures did not seem to be available, determinations were carried out with three different pieces of apparatus, namely: (1) a large glass dilatometer, with a bulb of capacity 61·287 c.c. at 0°, (2) a small quartz weight-thermometer, the volume of which at 0° was 8·63265 c.c., and (3) a large quartz dilatometer, with a bulb of capacity 56·74 c.c. at 0°.

In the case of the glass dilatometer, the cubical coefficient of expansion of the glass was determined and found to be 0·0000258. The coefficient of expansion of the fused silica ware used was taken as 0·00000177. The table on p. 909 gives a summary of the values obtained.

The agreement of the different series seems fairly satisfactory, but it must be noted that they are not in accord with much of the previously published results. For example, Ossan (*Ann. Phys. Chem.*, 1834, [ii], **31**, 33) gives a density of 1·927 at 115°, Rudge (*Proc. Camb. Phil. Soc.*, 1910, **16**, 59) 1·861 for 133°, and Ramsay (T., 1879, **35**, 471) gives 1·4578 to 1·513 as the density at the boiling point. Space considerations prevent discussion of earlier work, but it might be noted that Kruyt (*Zeitsch. physikal. Chem.*, 1908, **64**, 513) gives a useful bibliography.

The peculiar variation of the coefficient of expansion towards 160° seems to point to an alteration of molecular complexity.

TABLE I.

Density of Sulphur. Collective Table of Results.

Temperature.	Series I. Glass dilatometer (c = calculated).	Series II. Quartz weight-thermometer (c = calculated).	Series III. Quartz dilatometer.	Coefficients of expansion of sulphur calculated from Series III.	
				Temp. range.	Mean coefficients.
115·1°	1·8094	1·8086	1·8084	—	—
122·2	1·8030 c.	1·8028	—	—	—
134·0	1·7921	1·7931	1·7938	115 —134°	0·000430
138·2	1·7877 c.	1·7896 c.	1·7905	134 —138·2	0·000439
145·5	1·7807	1·7839 c.	1·7846	138·2—145·5	0·000465
151·5	1·7761	1·7791 c.	1·7794	145·5—151·5	0·000487
156·9	1·7722 c.	1·7747	1·7747	151·5—156·9	0·000490
158·5	1·7710	1·7739 c.	1·7739	156·9—158·5	0·000282
161·0	1·7704	1·7733 c.	1·7733	158·5—161·0	0·000135
165·0	1·7695 c.	1·7724 c.	1·7724	161·0—165·0	0·000127
171·3	—	1·7705 c.	1·7705	165·0—171·3	0·000170
178·3	1·7652 c.	1·7681 c.	1·7681	171·3—178·3	0·000194
184·0	1·7632	1·7648	1·7651	178·3—184·0	0·000298
210·0	1·7505	1·7510	1·7511	184·0—210·0	0·000308
239·5	1·7307	1·7340	1·7341	210·0—239·5	0·000344
278·5	1·7072	1·7119	1·7097	239·5—278·5	0·000366
357·0	1·6565	1·6563	1·6620	278·5—357	0·000366
445·0	1·5994	1·6047	1·6140	357 —445	0·000338
—	—	Separate experiment	1·6102	357 —445	0·000366

The relationship of density to temperature is well expressed in curve No. 1, which shows clearly the peculiar bend, beginning at about 160°, and resulting in a complete alteration of alignment.

Determination of Surface Tension and Molecular Complexity of Sulphur.

The values for surface tension obtained in the different series of experiments with the seven capillary tubes mentioned above may be most conveniently considered with regard to sulphur between two ranges of temperature:

Part I. Mobile sulphur (S_λ), 115° to 160°.
Part II. Viscous sulphur (S_μ), 160° to 445°.

This division is rendered advisable, because of the extraordinary variations in the viscosity of sulphur. Between 115° and 160°, the viscosity varies only slightly, being given by Rotinjanz (*Zeitsch. physikal. Chem.*, 1908, **62**, 609) as 11 at 120° and 8 at 150°. The viscosity of water at 100° is 0·0028, so that sulphur near its melting point is about 4000 times more viscous than water at its boiling point. At approximately 160°, however, there is a sudden alteration of viscosity, which greatly increases. The augmentation continues up to about 187°, at which temperature Rotinjanz gives the viscosity as 52,000, that is to say, 18,600,000 times greater than water at 100°. Above 190°, the viscosity diminishes, becoming 13,300 at 240° and 74 at the boiling point. It is doubtful, however, whether Rotinjanz was working with pure sulphur.

Part I.

Determination of the Surface Tension, Molecular Surface Energy, and Molecular Complexity of Mobile Sulphur (S_λ), 115—160°.

The results obtained with the capillary tube of approximately 1 mm. bore might be summarised as typical, although presumably not quite so accurate as those determined with narrower tubes. The difficulty of obtaining correct values depends primarily on the impossibility of reading with absolute accuracy the depth of the meniscus at the surface of the liquid in the vessel. The accuracy is generally within 0·01 cm., and the possible error would be less if the capillary tube were aligned so as to be exactly in the centre of the experimental tube.

TABLE II.

Summary of Results of Four Series of Experiments with Capillary Tube No. 3. (Radius, 0·05208 cm.)

Temperature.	116·4°	132°	142·8°	155·6°
Capillary rise in cm.	1·27 : 1·27	1·24 : 1·24	1·225 : 1·225	1·19 : 1·20
	1·27 : 1·27	1·24 : 1·24	1·225 : 1·225	1·19 : 1·19
	1·27 : 1·27	1·24 : 1·24	1·225 : 1·225	1·20 : 1·20
Average capillary rise (cm.)	1·27	1·24	1·225	1·195

From such results, the surface tension can be calculated by working from the general equation usually employed, namely, $\gamma \times 2\pi r \times \cos\theta = \pi r^2 \times (h + r/3) \times (d - d_1) \times g$, where γ is the surface tension, r the radius of the capillary tube, h the capillary rise, $r/3$ the correction for capillary meniscus, d the density of the liquid, d_1 the density of any gas above the liquid, and g the acceleration of gravity. The density of the vapour (d_1) can usually be safely neglected, and since molten sulphur wets glass, $\cos\theta$ may be taken as unity.

As previous workers have assumed that there is a definite contact angle between sulphur and glass, and Rudge (*Proc. Camb. Phil. Soc.*, 1910, **16**, 55) has determined the angle by two methods to be 60°, the author has summarised his reasons for the above conclusion in a separate paper, and need only record here that the behaviour of sulphur during purification seems decisively to negative anything more than a very small contact angle.

In the case of pure fused sulphur, large bubbles of gas in the capillary tube were, as already noted, cylindrical with hemisperical ends, and bubbles of the same diameter as the capillary tube or smaller were apparently spheres, and the contact angle seemed to be zero, the sulphur appearing to wet the glass. In the case of impure sulphur, these relationships did not hold. There seemed to be inconstant contact angles, which might differ considerably in different parts of the same capillary tube, and often approximated to 90°. The diagram on p. 912 (Fig. 3) gives an idea of the nature of the bubbles in the two cases.

The change in form of the bubbles as represented for impure and pure material was invariably accompanied by a great increase of surface tension, which might nearly double or triple in a very short time, and then seemed to remain absolutely constant for a given temperature.

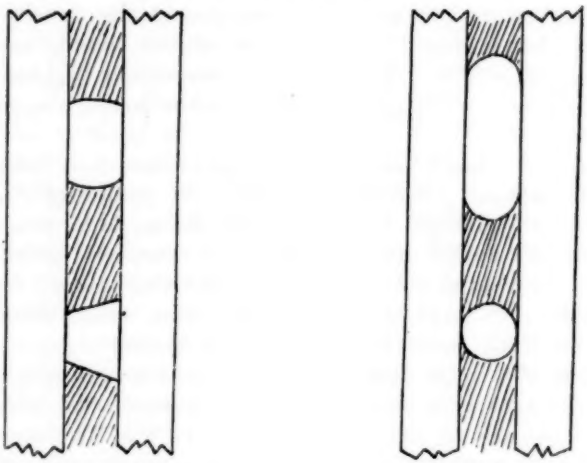
It might also be pointed out that a contact angle of 60° is improbable for two other reasons. In the first place, it would mean multiplying the values of surface tension summarised below

by 2, which would raise the surface tension of sulphur for temperatures above 115° to more than double that of water. In the second place, if the contact angle between sulphur and glass were 60°, the formula deduced from the variation of molecular surface energy with temperature could be represented at S_2, which, in view of the known aggregations of sulphur in the gaseous state and in solution, seems quite inadmissible.

Assuming the angle of contact between sulphur and glass to be zero, the values obtained for surface tension and molecular surface energy are summarised in table III (p. 913).

The mean of the above eleven values for the differential coefficient, K_1, is 1·008, which would give 3·05 as the multiplying

FIG. 3.



Impure sulphur. *Pure sulphur.*

factor for S_2. It must be noted, however, that capillaries Nos. 1 and 2, of diameters 2 and 1·5 mm. approximately, were primarily employed for exploratory purposes in connexion with viscous sulphur, and the results are given in order to show that such capillary tubes are rather wide for accurate work, and the values obtained should not be included in any general averages. Excluding these determinations of K_1, the mean of the remaining nine series is 1·03, which gives 2·96 as the average value for x. Four of these values of K_1 represent, however, comparatively small temperature limits, and what is required here is an average value of K_1 for the whole range of temperature during which sulphur remains mobile after melting, that is to say, for the range

TABLE III.

Mobile Sulphur (S_λ).

Variation of Surface Tension and Molecular Surface Energy with Temperature.

Capillary No.	Temperature.	Series.	Radius of capillary. r	Mean capillary rise in cm. $h + r/3$.	Density of sulphur.	Surface tension in dynes. $\gamma = r/2(h+r/3)$dg.	Molecular surface energy in ergs. $\gamma(Mv)^{\frac{1}{3}}$.	K_1.	Factor for multiplication of S_2. x.
3	116·4°	A	0·05212	1·287(4)	1·807	59·48	642·4	A & B = 1·04	
	132·0	B	0·05213	1·257(4)	1·795	57·72	626·1	A & C = 0·94	3·06
	142·8	C	0·05214	1·242(4)	1·787	56·77	617·7	A & D = 1·04	
	155·6	D	0·05214	1·212(4)	1·776	55·08	601·6		
4	118·8	A	0·03321	2·031	1·805	59·73	645·5	A & B = 1·14	2·85
	144·2	B	0·03322	1·946	1·786	56·65	616·5	A & C = 0·97	
	155·8	C	0·03322	1·928	1·776	55·82	609·6		
5	118·0	A	0·02364	2·933	1·806	61·44	663·6	A & B = 1·05	
	144·6	B	0·02365	2·820	1·785	58·39	635·7	A & C = 1·03	2·91
	155·6	C	0·02365	2·776	1·776	57·22	624·8		
6	121·5	A	0·01523	4·502	1·804	60·67	656·0	A & B = 1·00	3·09
	156·3	B	0·01524	4·284	1·775	56·84	621·2		
7	122·2	A	0·008957	7·695	1·803	60·96	659·4	A & B = 1·07	2·79
	156·9	B	0·00896	7·296	1·775	56·94	622·2		
1	112·0	A	0·10004	0·655	1·810	58·20	627·7	A & B = 0·89	3·68
	158·0	B	0·10008	0·619	1·773	53·89	589·3		
2	117·6	A	0·07216	0·874	1·806	55·89	603·7	A & B = 0·92	3·50
	156·3	B	0·07219	0·827	1·775	51·99	568·0		

115° to 160° inclusive. Average values of molecular complexity for this range can be computed from table IV (p. 915).

These average values for the multiplying factor seem clearly to indicate that it is approximately 3, and therefore a minimum of 95 per cent. of sulphur between 115° and 160° must have a molecular complexity represented by the formula S_6. If the Ramsay and Shield's method of calculation be invalid, then the value of S_6, indicated from above results, would be merely a coincidence, but, if so, it is a remarkable one. The analogy to aggregates of C_6 is obvious.

Part II.—Determination of the Molecular Complexity of Viscous Sulphur. Temperature Range, 160—445°.

It has been already stated that at approximately 160° there is a sudden increase of viscosity, which, according to Rotinjanz, attains a maximum of 52,000 about 190°. The enormous viscosity during the earlier part of the temperature range considered (160° to 220°) causes difficulty in carrying out the experiments. The time required may be considerable; for example, at 183°, even with a tube of 1 mm. diameter, the time taken by the sulphur in falling the last 0·5 cm. was more than three hours, and in the case of the capillary of radius 0·03318 cm., the time taken to fall 0·5 cm. was about twenty hours, and the final readings were taken twenty-five hours after the capillary was raised into position. Presumably time of fall $\propto 1/r^4$, and therefore only tubes above 0·02 cm. radius can be conveniently used for the range 165—220°.

A summary of the results obtained is given in table V (p. 916).

As a preliminary to the consideration of the above results, the variation of surface tension from melting point to boiling point might be represented by a curve in a typical case. Curve No. 2 (Fig. 4, p. 917) shows the relationships graphically, and indicates that the surface tension as such seems not to be affected by the viscosity, and falls in two confluent phases from melting point to boiling point. The remarkable analogy of this curve to that expressing the variation of density with temperature is evident.

As regards the molecular complexity of viscous sulphur, considering the results for capillaries 3 and 4, which, as previously pointed out, are alone valid, the variations of multiplying factor for S_2 are between 6·8 and 14·3, which would correspond with S_{14} and S_{28} or S_{29} respectively. It must be noted, however, that the only high values are between 160° and 183·5°, where the variations of capillary rise are so small as to be within the limits of error, and

TABLE IV.

Mobile Sulphur (S_λ).

Capillary No.	Temperature range.	Variation of capillary rise $h+r/3$.	Variation of surface tension. (Dynes.)	Variation of molecular surface energy. (Ergs.)	K_1.	Factor for multiplication of S_2.
3	116·4—155·6°	1·287—1·212	59·48—55·08	642·4—601·6	1·04	2·91
4	118·8—155·8	2·031—1·928	59·73—55·82	645·5—609·6	0·97	3·23
5	118·0—155·6	2·933—2·776	61·44—57·22	663·6—624·8	1·03	2·96
6	121·5—156·3	4·502—4·284	60·67—56·84	656·0—621·2	1·00	3·09
7	122·2—156·9	7·695—7·296	60·96—56·94	659·4—622·2	1·07	2·79
Average	119·4—156·04	—	60·46—56·38	653·4—615·9	1·02	2·996

TABLE V.

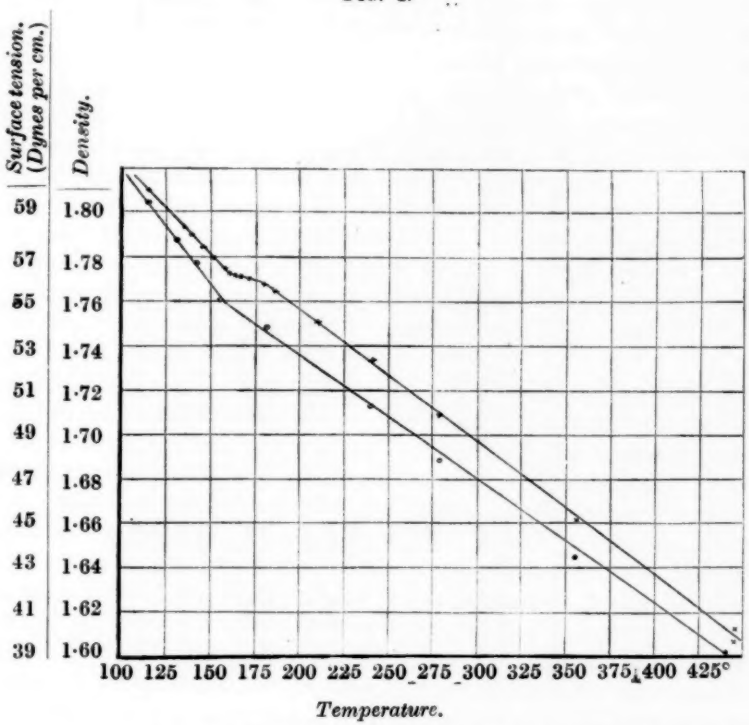
Viscous Sulphur (S_μ).

Variation of Surface Tension and Molecular Surface Energy with Temperature.

Capillary No.	Temperature.	Series.	Radius of capillary r.	Mean capillary rise in cm. $h+r/3$.	Density of sulphur.	Surface tension in dynes $\gamma=r/2(h+r/3)$dg.	Molecular surface energy in ergs $\gamma(Mv)^{\frac{1}{3}}$.	Differential coefficient K_1.	Factor for multiplication of S_μ. (x).
1	158°	A	0·10008	0·619	1·773	53·89	589·3	A & B=0·53	8·0
	445·0	B	0·10033	0·473	1·605	37·37	436·7		
2	156·3	A	0·07219	0·827	1·775	51·99	568·0	A & B=0·47	9·59
	445·0	B	0·07236	0·644	1·605	36·69	428·8		
3	155·6	A	0·05214	1·212(4)	1·776	55·08	601·6	A & B=0·36	14·3
	183·5	B	0·05216	1·194	1·765	53·93	591·6		
	239·5	C	0·05218	1·137	1·734	50·47	559·5	A & C=0·5	8·74
	280·0	D	0·05220	1·092	1·710	47·80	535·6	C & D=0·59	6·8
	357·0	E	0·05223	1·027	1·657	43·60	498·9	C & E=0·52	8·2
	445·0	F	0·05227	0·947	1·605	38·97	455·5	C & F=0·51	8·2
4	155·8	A	0·03322	1·928	1·776	55·82	609·6	A & B=0·37	13·7
	183·5	B	0·03323	1·901	1·765	54·69	599·2	A & C=0·50	8·74
	211·0	C	0·03324	1·851	1·751	52·83	582·0		
	241·0	D	0·03324	1·786	1·734	50·51	560·6	A & D=0·57	7·18
	280·0	E	0·03325	1·741	1·710	48·56	544·1	D & E=0·43	10·9
	302·0	F	0·03326	1·706	1·699	47·31	532·1	D & F=0·47	9·59
	357·0	G	0·03328	1·636	1·657	44·27	506·5	D & G=0·47	9·59
	445·0	H	0·03330	1·521	1·605	39·87	466·0	D & H=0·46	9·90

therefore, for sulphur of very great viscosity, it would be inadvisable to lay any stress on values calculated for a short range of temperature. One should nevertheless be able to deduce approximations for long ranges of temperature, and to decide whether the complexity remains nearly unaltered or undergoes distinct variation between 160° and 445°, provided that the Ramsay and Shield's method of calculation can be used for extensive ranges.

FIG. 4.



Upper curve (*No.* 1) *shows the variation of the density of sulphur with temperature.*
Lower curve (*No.* 2) *shows the variation of the surface tension with temperature.*

A consideration of the values obtained for the following four temperature limits should give sufficient material for deduction of conclusions: (*A*) 160° to 211° and 240°, (*B*) 240—357°, (*C*) 357—445°, (*D*) 160—445°.

The molecular complexity for temperature ranges of 80° or more varies between S_{14} and S_{20}, and for still longer ranges seems to approximate to S_{18}. Although the above results can only be

TABLE VI.

Molecular Complexity of Viscous Sulphur (S_μ).

Temperature range.	Capillary No.	Variation of capillary rise in cm.	Variation of molecular surface energy in ergs.	Differential coefficient K_1.	Deduced value of x.	Number of atoms in the sulphur molecule.	
155·6—239·5°	3	1·212—1·137	601·6—559·5	0·50	8·74	17–18	
155·8—211	4	1·928—1·851	609·6—582·0	0·50	8·74	17–18	16
155·8—241	4	1·928—1·786	609·6—560·6	0·57	7·18	14	
239·5—357	3	1·137—1·027	559·5—498·9	0·52	8·24	16–17	
241 —357	4	1·786—1·636	560·6—506·5	0·47	9·59	19	18
211 —357	4	1·851—1·636	582·0—506·5	0·52	8·24	16–17	
357 —445	3	1·027—0·947	498·9—455·5	0·49	9·00	18	
	4	1·636—1·521	506·5—466·0	0·46	9·90	20	
160 —445	1	0·618—0·473	587·3—436·7	0·53	8·00	16	
	2	0·826—0·644	564·0—428·8	0·47	9·59	19	
	3	1·212—0·947	597·6—455·5	0·50	8·74	17–18	
	4	1·927—1·521	605·4—466·0	0·49	9·00	18	

regarded as first approximations, the similarity of the values obtained seems sufficient to justify the assumption that near 160° sulphur polymerises to form a complex S_{18}, which remains stable up to near the boiling point. The equation representing the transformation in the neighbourhood of 160° would therefore be represented by the symbols $3S_6 \rightleftarrows (S_6)_3$.

The alteration of orientation of the components of the molecule S_6 before and during polymerisation, might explain the peculiar variations of the coefficient of expansion already referred to. It would be easy to represent graphically complexes of S_{18}, which on decomposition near the boiling point might be supposed to give the aggregates S_6, S_8, and S_2, which, according to Preuner and Schupp (*Zeitsch. physikal. Chem.*, 1909, **68**, 129), are present in gaseous sulphur. In particular, their emphasis of the complex S_6 is in accord with the above results for the liquid state.

As regards other important researches, it is evident, however, that the value S_{18} for viscous sulphur (S_μ) cannot be regarded as in agreement with the conclusions of Smith and his collaborators, or others, who regard S_μ as S_6, but the author has no intention of considering fully what might be termed collateral work in this paper, as it would mean undue expansion.

It might perhaps be argued that if polymerisation occurs in the neighbourhood of 160°, then above 190° the proportion of S_μ found by rapid cooling should be constant. This need not necessarily be the case, however. The rapidity of the reverse change might be so great, even in the presence of substances like sulphur dioxide, which Smith has found to act here as a catalytic retarder, that only a small proportion of the complex aggregations could be caught and kept as such by cooling in ice; such aggregates would be in a strained position at the ordinary temperature. The complex molecules at high temperatures would be more easily preserved by rapid cooling, as there would not be time to alter the greater orientation of the atoms in the molecule or of the aggregates of S_6 with regard to each other. What is called plastic sulphur need not, therefore, be so homogeneous as S_{18} in the liquid state, but might consist of aggregates in slightly different conditions of strain. The polymerisation may depend on the lowering of the valency of sulphur with rise of temperature.

Determination of Surface Tension of Sulphur by other Observers.

The results of Zickendraht, Pisati, Capelle, and Rudge might be briefly commented on, but only those obtained by the first-named observer approximate at any temperature to those given above.

Near the melting and boiling points, the values of Zickendraht and the author are nearly concordant, but for viscous sulphur the results are quite different; for example, at 250° Zickendraht (*Ann. Physik*, 1906, [iv], **21**, 141) finds a surface tension of 118 dynes per cm., as against 50 dynes given in table V. It follows that above 160°, Zickendraht's curve showing the variation of surface tension with temperature rises and then falls abruptly in a very peculiar manner.

The results of an earlier observer, Pisati (*Gazzetta*, 1877, **7**, 357), are somewhat similar to those of Zickendraht. His surface-tension curves show a corresponding transverse wave.

A third experimenter, who found that the surface tension of sulphur increased with temperature, was Capelle (*Bull. Soc. chim.*, 1908, [iv], **3**, 764), who obtained a small increase of surface tension between 125° and 142°, and then a rapid increase between 142° and 160°. A few of the results obtained by Capelle, with approximate values calculated from table III, are as follows:

Temperature	125°.	135°.	142°.	152°.	160°.
Capillary rise (Capelle), cm....	2·08	2·08	2·10	2·50	2·74
Calculated values, cm.	5·47	5·39	5·33	5·24	5·18

It is evident that the curves representing these numbers differ both in degree and character.

Another research, where the presence of dissolved substances interfered, has been already referred to in connexion with angles of contact. Rudge (*loc. cit.*) stated that he found no change of surface tension with temperature between 122° and 154°, thus differing entirely from the observers already mentioned. The reason for this statement depends on the experimental error (0·075 cm.) for one temperature being greater than the variation of capillary rise should have been for 30° with the tube used ($r=0{\cdot}0515$ cm.; compare table III).

The mean value of capillary rise is given as 0·246 cm. at 133°, and the corresponding surface tension 11·56 dynes. The calculated values are 1·27 cm. and 59 dynes per cm. approximately.

The results of the above series of researches indicate conclusively that unless sulphur is nearly pure—the author makes no claim to have prepared absolutely pure sulphur—no definite values can be found for the surface tension.

The critical temperature can be calculated from the above values. $T_c=\frac{\gamma(Mv)^{\frac{2}{3}}}{K_1}+t+6°$, where t is the temperature of experiment. Two results are obtained, one pertaining to the complex S_6, namely, 766°, and the other corresponding with the aggregate S_{18}, namely, 1390°.

Other Methods of determining Molecular Complexity from Surface Tension Data.

The validity of the Ramsay and Shield's method of calculation as a means of determining molecular weight has been questioned. The values of molecular complexity or of constant (K) obtained from specific formulæ by a few other methods are summarised below.

(1) The specific cohesion (a^2) is 6·8 at 119·4°, instead of 4·3 as previously given, showing that sulphur does not obey Quincke's law. Walden and Dutoit and Moijou give $\frac{L_v}{a^2 \times 10^2} = 17{\cdot}9 = K$. The value of K for sulphur at 119·4° is 66, computing L_v as 450.

(2) Walden and Kistiakowsky state that $\frac{Ma^2 \times 10^2}{T} = 1{\cdot}162 = K$. M for sulphur by this method is 164·3, indicating a molecular complexity between 5 and 6.

(3) Dutoit and Moijou's empirical relationship between M, pressure (p) at the boiling point, and a^2 indicates for sulphur a molecular complexity of 6 to 7.

(4) Walden states that $\frac{Ma^{2\phi}}{T_\phi} = K = 3{\cdot}65$, where T_ϕ is the absolute melting point. Here the formula deduced for the melting point is S_6 (approximately).

(5) Walden gives $\frac{ML_\phi}{T_\phi} = K = 13{\cdot}3$. The molecular formula deduced for sulphur would be S_{14}.

(6) Longinèscu's method of calculation, $n = \left(\frac{T}{100d}\right)^2$ indicates a formula for S_{12} for the boiling point.

(7) Application of Trouton's rule, and Dunstan's method of calculation from viscosity, seem to point to a high molecular complexity.

All the above methods of calculation indicate considerable association. Whilst the complex S_6 is apparently corroborated in several calculations, yet the Ramsay and Shield's values seem to agree better with the experimental results.

Summary of Conclusions.

(1) Contrary to statements by various observers, the surface tension of liquid sulphur can be determined by means of capillary tubes between the melting point (115°) and the boiling point

(445°). Impurities (especially sulphuric acid, sulphur dioxide, and hydrogen sulphide) must be previously removed.

(2) Sulphur can be purified by distillation and subsequent boiling in dry nitrogen, the gases evolved being pumped off.

(3) *Surface Tension of Mobile Sulphur* (115—160°), S_λ.—A mean value for five capillary tubes gave surface tensions of 60·46 and 56·38 dynes, respectively, for 119·4° and 156°, the corresponding molecular surface energies being 653·4 and 615·9 ergs. The corresponding value of K_1 is 1·02, and the average multiplying factor for S_2 is 2·996 (approximately 3).

(4) The molecular complexity of at least 95 per cent. of mobile sulphur (S_λ) between 115° and 160° is presumably represented by the formula S_6, assuming the validity of the Ramsay and Shield's method of calculation.

(5) The angle of contact of sulphur and glass is taken as zero for reasons assigned.

(6) *Surface Tension of Viscous Sulphur* (160—445°), S_μ.—In disagreement with the results observed by other observers, the surface tension of sulphur falls continuously from the melting point to boiling point, being 48·2 dynes at 280° and 39·4 dynes at 445°.

(7) The molecular complexity alters about 160°, and it might be stated as a first approximation that an endothermic termolecular polymerisation appears to occur near that temperature, $3S_6 \rightleftharpoons (S_6)_3$. The aggregate S_{18} seems to be stable up to near the boiling point.

(8) The polymerisation may be due to a tendency of sulphur to lower its valency with rise of temperature, the complex S_6 possessing a residual valency at 160°.

(9) Other methods of calculation of molecular complexity seem to emphasise the aggregate S_6, but the results do not seem to accord with experimental averages so well as those of the Ramsay and Shield's method.

(10) Calculations of critical temperature give two variant values depending on temperature of calculation. Above 160°, the value found is 1390°, corresponding with the complex S_{18}. Below 160°, the inadmissible value of 766° is obtained, corresponding with S_6.

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LXXXIV.—*The Freezing Points of Mixtures of Phenol, o-Cresol, m-Cresol, and p-Cresol.*

By Harry Medforth Dawson and Christopher Archibald Mountford.

In connexion with some experiments which were undertaken with the object of devising a method for the estimation of the residual phenol in commercial cresylic acids, the authors were led to the consideration of the question of the application of physical methods in the analysis of mixtures of chemically similar substances such as are presented by mixtures of phenol and its homologues.

Although, in general, homologous substances can be separated by fractional distillation, this method is less widely applicable to the separation of isomerides. The tar acids obtained by the distillation of coal consist for the most part of phenol, cresols, and xylenols, and on the basis of the boiling-point differences it is possible to separate the complex mixture of tar acids into fractions which consist for the most part of (1) phenol, (2) *o*-cresol, (3) *m*-cresol and *p*-cresol, (4) xylenols, etc.

In the absence of any large demand for pure cresol fractions, commercial fractionation is usually limited to the production of distillates rich in phenol, from which carbolic crystals may be obtained by crystallisation, and of fractions of higher boiling point containing little phenol and consisting mainly of the three cresols mixed with xylenols. The efficiency of commercial fractionating plants varies very considerably, and although it has been found possible to realise the above series of fractions by the use of suitable fractionating columns, this result has not been generally aimed at and is by no means frequently attained. Mixtures of phenol and its homologues are therefore not only met with in the course of the complex fractionation processes, which are not infrequently regarded as being of the nature of trade secrets, but appear also as the finished products of the tar distiller.

Such products offer an interesting analytical problem, and the authors have had in mind the application of their results to this problem in proceeding to the investigation of the quaternary system having phenol and the three isomeric cresols as its components.

The fact that three of these components are isomerides and homologous with the fourth involves not only a close correspondence in their chemical behaviour, but also a degree of approximation in their physical properties that narrows very considerably

the foundation on which a method for the estimation of the several components in any given mixture may be built up.

Preliminary experiments showed that the freezing-point relations were likely to be of the greatest value in connexion with the analytical problem, and for this reason we have made a detailed examination of the freezing points of the six possible binary combinations, as well as of certain ternary and quaternary mixtures.*

The phenol and cresols used in the investigation were purified by distillation and crystallisation. The phenol was obtained from a commercial sample of carbolic crystals, whilst the *m*-cresol and *p*-cresol were synthetic products. In the case of *o*-cresol, observations were made in part with a purified commercial sample and in part with a substance of synthetic origin. The hygroscopic nature of all four substances demands the utmost care in manipulation, and special precautions were taken to eliminate the last traces of water from all the materials which were used in the freezing-point determinations. For the removal of water, it was found most convenient to heat the substance in a retort for two or three hours, the supply of heat being regulated so that, during this time, from 5 to 10 per cent. of the substance distilled over. The residual liquid was then immediately transferred to a dry, well-stoppered bottle.

The actual data which are recorded in the paper represent the results of observations of the lowest temperatures at which the various mixtures undergo complete liquefaction. Weighed quantities of the components were introduced into glass tubes about 10 cm. long and 1 cm. in diameter, the tubes being carefully sealed with due regard for the necessity of avoiding the introduction of water vapour during the process. A preliminary and approximate determination of the temperature of complete liquefaction was then made, after which the mixture was again solidified and the melting-point tube attached diametrically to a rotating wheel supported in a large water-bath, the temperature of which could be raised very slowly. During this process, the contents of the tube were thoroughly mixed and the temperature at which the

* Since this paper was submitted to the Chemical Society, a communication on the same subject has been published by Fox and Barker (*J. Soc. Chem. Ind.* 1918, **37**, 268). The results obtained by these observers differ very considerably from those recorded in the present paper. The discrepancies would appear to be mainly due to the circumstance that the workers in the Government laboratory have made use of a method for the determination of the freezing points which does not give satisfactory results for many of the mixtures examined, whilst it would seem that the substance they have assumed to be pure *m*-cresol consists of a mixture of about 85 per cent. of *m*-cresol and 15 per cent. of *p*-cresol.

last crystals disappeared was registered. In virtue of the preliminary measurement, it was possible to set the temperature of the water-bath about 1—2° below the temperature to be measured, and to adjust the heat supply so that the temperature rose very slowly. In the case of the mixtures of higher melting point, the temperature of complete liquefaction could be determined in this way within ±0·05°, but at the lowest temperatures the precision of the measurements was not quite so great. The temperatures at which liquefaction is complete correspond with those at which crystallisation of the liquid would begin in the absence of supercooling, and in what follows these temperatures will be referred to as freezing points. It should be mentioned that the crystallisation of certain mixtures does not occur at all readily. This is particularly noticeable in the case of mixtures which contain a large proportion of *m*- or *p*-cresol, and inoculation of the supercooled liquids was occasionally found to be necessary to start crystallisation.

Before proceeding to give the results of our experiments, it may be appropriate to refer to the considerable discrepancies between the values recorded for the melting point of phenol and the cresols in the literature. We have made no attempt to reconcile these divergent numbers, and the freezing-point data recorded in this paper are not put forward with any suggestion that the phenols were absolutely pure, although all reasonable precautions were taken in regard to their purification.

In reference to the tables in which the experimental data are recorded, it may be noted that the composition of those binary mixtures which contain phenol is expressed in terms of both weight percentage and molecular percentage. For mixtures of cresols,

TABLE I.

Phenol and o-Cresol.

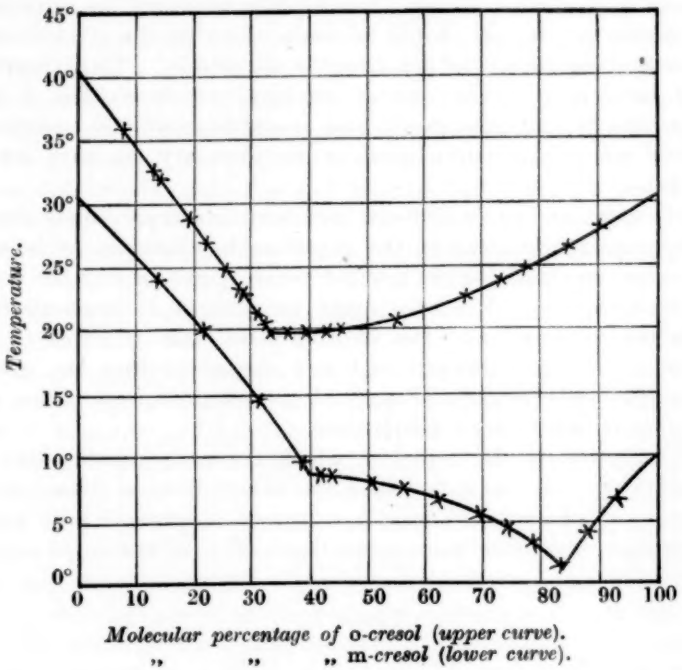
Weight per cent. cresol.	Mol. per cent. cresol.	F. p.	Weight per cent. cresol.	Mol. per cent. cresol.	F. p.
0	0	40·5°	36·96	33·78	19·7°
9·00	7·93	35·8	39·43	36·16	19·9
14·72	13·06	32·6	42·47	39·12	19·85
15·82	14·06	32·05	46·10	42·68	19·85
21·46	19·22	28·7	48·81	45·35	19·95
24·54	22·06	27·05	58·63	55·23	20·75
28·28	25·55	24·65	69·70	66·69	22·5
30·69	27·82	23·1	75·75	73·11	24·05
31·84	28·9	23·0	80·00	77·69	24·85
34·27	31·21	21·15	86·93	85·11	26·7
34·54	31·47	21·2	91·41	90·25	27·95
36·00	32·87	20·55	100	100	30·45

the two series are, of course, identical. In the freezing-point diagrams which have been constructed from the experimental data, the composition of the mixtures is plotted in terms of the molecular percentage.

The freezing-point curves for mixtures of phenol and *o*-cresol (upper curve in Fig. 1) appear to consist of two branches corre-

FIG. 1.

Phenol and o-*cresol.*
o-*Cresol and* m-*cresol.*



Molecular percentage of o-*cresol* (*upper curve*).
" " " m-*cresol* (*lower curve*).

sponding with two series of mixed crystals. Starting from the eutectic, the *o*-cresol branch shows very little change in the freezing point up to about 50 mols. per cent. of *o*-cresol, and for this reason it is scarcely permissible to deny the possibility that there is an intermediate branch corresponding with a compound. There is, however, no clear evidence of compound formation in the case of this particular binary combination.

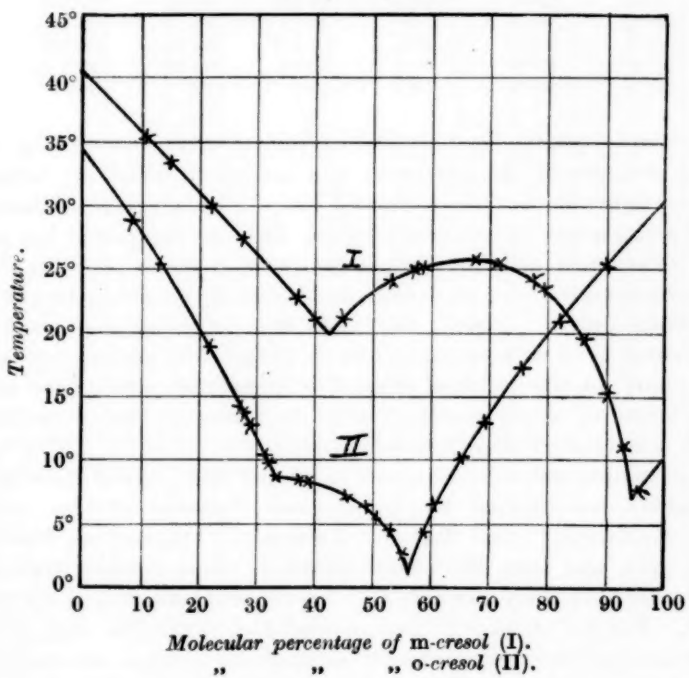
TABLE II.

Phenol and m-*Cresol.*

Weight per cent. cresol.	Mol. per cent. cresol.	F. p.	Weight per cent. cresol.	Mol. per cent. cresol.	F. p.
0	0	40·5°	61·93	58·59	25·05°
11·73	10·32	35·4	70·25	67·24	25·8
16·26	14·35	33·55	74·36	71·62	25·25
24·23	21·75	29·95	79·72	77·37	24·2
29·83	26·96	27·4	81·94	79·80	23·1
39·98	36·66	22·8	87·54	85·92	19·5
43·44	40·00	21·1	91·52	90·37	15·2
48·37	44·92	21·6	93·72	92·85	11·2
56·54	53·07	24·0	95·89	95·31	7·6
60·40	57·01	24·95	100	100	10·0

FIG. 2.

Phenol and m-*cresol.*
o-*Cresol and* p-*cresol.*



Molecular percentage of m-*cresol* (I).
" " " o-*cresol* (II).

The freezing-point curves for mixtures of phenol and *m*-cresol (see Fig. 2, curve I) are well defined, and show clearly the formation of a compound containing one molecule of phenol in combination with two molecules of *m*-cresol. The flatness of the curve

suggests that the compound is very considerably dissociated in the liquid state. The compound melts at about 25·9°, and the eutectic mixtures which are characteristic of this binary system correspond with 44·8 and 95·2 per cent. by weight of *m*-cresol, the corresponding temperatures being 20·2° and 7·3°.

TABLE III.

Phenol and p-*Cresol.*

Weight per cent. cresol.	Mol. per cent. cresol.	F. p.	Weight per cent. cresol.	Mol. per cent. cresol.	F. p.
0	0	40·5°	53·90	50·45	0·1°
12·50	11·06	32·35	57·50	54·06	0·75
20·04	18·00	26·8	60·55	57·17	0·8
24·50	22·02	23·9	62·88	59·59	4·65
29·07	26·27	19·6	68·18	65·10	10·0
33·76	30·75	15·25	76·27	73·67	16·55
38·21	34·92	11·05	79·60	77·25	19·5
42·45	39·07	6·65	83·63	81·64	22·3
43·22	39·83	4·9	84·17	82·23	22·75
45·11	41·70	2·5	91·47	90·32	28·15
47·37	43·93	0·2	96·06	95·49	31·2
49·77	46·33	−1·4	100	100	34·15

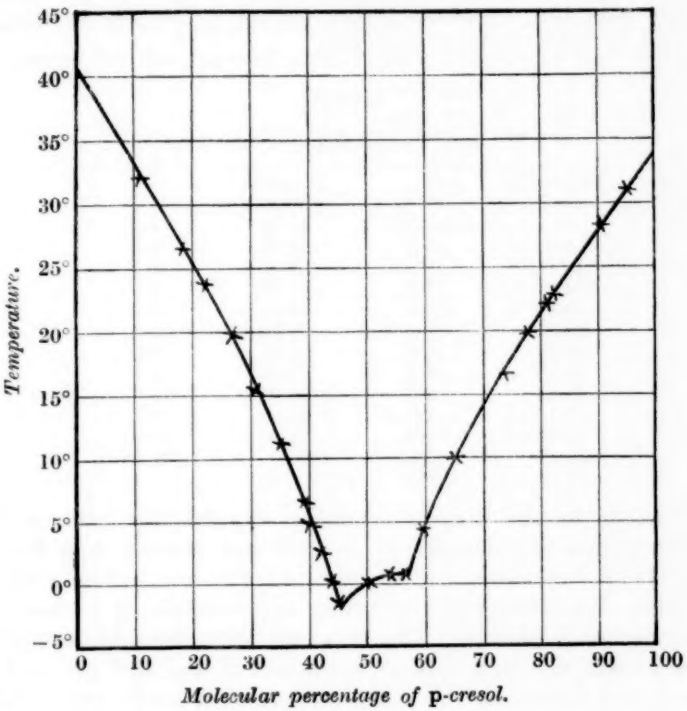
The curve system for mixtures of phenol and *p*-cresol (Fig. 3) affords evidence of the formation of a compound which crystallises at low temperatures from a limited range of mixtures. Although the freezing-point curve corresponding with the compound has not been determined with the desired precision, it seems probable that the compound contains one molecule of phenol in combination with two molecules of *p*-cresol, and that the corresponding curve is terminated by a eutectic point on the phenol side and by a transition point on the *p*-cresol side. The compound crystallises only from mixtures which contain phenol in excess of that proportion which is characteristic of the compound itself.

The freezing points of mixtures of phenol and *p*-cresol have been previously investigated by Lunge and Zschokke (*Chem. Ind.*, 1885, 6; Lunge, "Coal Tar and Ammonia," 5th edition, Part I, 1916, 277), and from the results obtained, these authors drew the conclusion that there are only two curves which meet in a eutectic point. Fox and Barker (*J. Soc. Chem. Ind.*, 1917, **36**, 842), without recording their experimental data, claim to have obtained the same result. In regard to this discrepancy, we would point out that our experimental numbers differ very widely from those of Lunge and Zschokke in the case of mixtures which contain an excess of phenol, and there can be no doubt whatever that the measurements of these authors involve errors of large magnitude.

On the other hand, if the data recorded by Lunge and Zschokke are plotted, the distribution of the points is such as to suggest the existence of an intermediate freezing-point curve, although these

FIG. 3.

Phenol and p-cresol.



authors interpreted these data in favour of a curve system consisting of two branches.

TABLE IV.

o-*Cresol and* m-*Cresol*.

Per cent. *m*-cresol.	F. p.	Per cent. *m*-cresol.	F. p.
0	30·45°	62·80	6·5°
13·74	23·95	69·28	5·8
21·69	20·00	74·39	4·6
31·31	14·6	78·69	3·6
38·75	9·4	83·25	1·7
41·64	8·5	88·02	4·3
43·68	8·3	93·39	6·6
50·64	7·9	100	10·0
56·14	7·6		

The diagrammatic representation of the data obtained for mixtures of *o*-cresol and *m*-cresol (lower curve in Fig. 1) points to the formation of a compound containing two molecules of *o*-cresol in combination with one molecule of *m*-cresol. The curve corresponding with the compound ends on the *o*-cresol side in a transition point at 8·5° and about 40 per cent. of *m*-cresol, whilst on the *m*-cresol side the compound curve terminates in the eutectic at 1·5° and 83·7 per cent. of *m*-cresol.

TABLE V.

o-*Cresol and* p-*Cresol.*

Per cent. *p*-cresol.	F. p.	Per cent. *p*-cresol.	F. p.
0	30·45°	61·02	8·5°
9·94	25·3	62·76	8·6
17·91	20·85	66·70	8·7
24·27	17·2	67·88	9·8
30·40	13·0	68·40	10·3
34·91	10·1	70·99	12·6
39·36	6·5	71·84	13·6
41·42	4·4	72·60	14·1
44·41	2·5	78·44	18·9
47·11	4·6	87·00	25·3
49·42	5·5	91·70	28·45
51·17	6·4	100	34·15
54·04	7·0		

According to the diagram showing the relation between the freezing points of mixtures of *o*-cresol and *p*-cresol (see Fig. 2, curve II), it is evident that chemical combination occurs with the formation of a compound containing one molecule of *o*-cresol and two molecules of *p*-cresol. The curve for the compound terminates on the *o*-cresol side in a eutectic point at 1·2° and 43·7 per cent. of *p*-cresol, and intersects the *p*-cresol curve at a point which corresponds very nearly with the composition of the compound. The plot of the experimental results does not permit of any definite statement with respect to the nature of the point of intersection,

TABLE VI.

m-*Cresol and* p-*Cresol.*

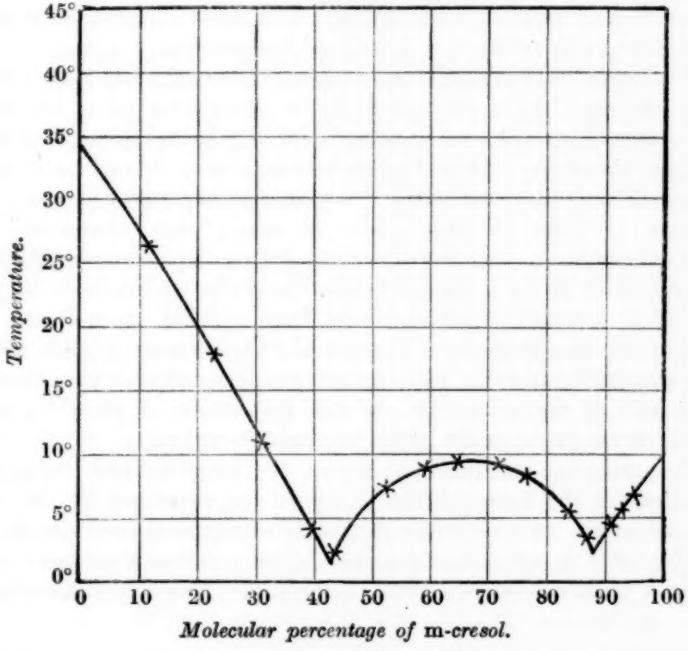
Per cent. *p*-cresol.	F. p.	Per cent. *p*-cresol.	F. p.
0	10·0°	41·22	8·8°
5·10	6·7	47·99	7·4
6·74	5·4	56·39	2·4
9·13	4·4	60·38	4·2
13·40	3·5	68·41	11·0
16·50	5·6	77·03	18·0
23·48	8·2	88·39	26·5
28·41	9·2	100	34·15
35·71	9·5		

but it is evident that the melting point of the compound is approximately 8·7°.

The freezing-point diagram for this pair of isomerides (Fig. 4) shows clearly the formation of a compound containing two molecules of *m*-cresol and one molecule of *p*-cresol. The relations exhibited resemble closely those which are shown by mixtures of *m*-cresol and phenol, and the compounds formed in the two cases contain the same proportion of *m*-cresol. The compound curve is terminated on the *m*-cresol side by the eutectic at 2·0° and 12·0

FIG. 4.

m-Cresol and p-*cresol.*



per cent. of *p*-cresol, and on the *p*-cresol side by the eutectic at 1·2° and 57·0 per cent. of *p*-cresol.

Although the diagrams which have been described afford a general survey of the equilibrium relations in the several binary systems, it is of interest to compare the changes which are produced in the freezing point of each of the four components when the three others are separately added. In making this comparison, it is more convenient to express the composition in terms of weight percentage. The advantage attaching to the weight percentage freezing-point curves is obvious when it comes to the application

of the freezing-point relations, and it need only be pointed out that when phenol is one of the two components, the curves in question will be slightly different from those shown in Figs. 1, 2, and 3.

Depression of the Freezing Point of Phenol by the Addition of o-, m-, *and* p-*Cresol.*

The depression of the freezing point of phenol produced by a given weight of cresol varies considerably according to the relative position of the methyl and hydroxyl groups in the cresol molecule. This is evident from the numbers in the following table (VII), which gives the freezing points of phenol–cresol mixtures containing 10, 15, 20, 25, 30, 35, and 40 per cent. by weight of *o*-cresol, *m*-cresol, and *p*-cresol respectively. The table shows that *m*-cresol produces the least effect and *p*-cresol the greatest.

According to Eykman's observations (*Zeitsch. physikal. Chem.*, 1899, **4**, 497), the molecular value of the depression of the freezing point of phenol which is produced by the addition of *p*-cresol is appreciably less than the value calculated from van't Hoff's formula, and also less than the average depression for a large number of different substances. It would seem, therefore, that solid solutions in phenol are formed by all three cresols, although the tendency to form these solutions increases considerably in passing from *p*-cresol to *o*-cresol and from *o*-cresol to *m*-cresol. On account of the divergence between the three freezing-point curves, it is impossible to make use of the freezing point of a phenol–cresol mixture for the estimation of the proportion of phenol present unless the nature of the admixed cresol is known.

The table in question also shows the results which have been obtained in the investigation of the effects produced by the addition of mixed cresols, and more particularly of mixed cresols containing only *m*-cresol and *p*-cresol. The numbers have been interpolated from curves representing the actual freezing-point data.

TABLE VII.

Freezing Points of Phenol–Cresol Mixtures.

Nature of added cresol.	10 per cent. cresol.	15 per cent. cresol.	20 per cent. cresol.	25 per cent. cresol.	30 per cent. cresol.	35 per cent. cresol.	40 per cent. cresol.
m-Cresol	36·2°	34·0°	31·8°	29·6°	27·3°	25·0°	22·6°
o-Cresol	35·1	32·4	29·6	26·75	23·75	—	—
p-Cresol	33·8	30·4	26·8	23·1	19·0	14·4	9·5
m- + *p*-Cresol = 2 : 1	35·1	32·4	29·6	26·75	23·75	20·75	17·5
m- + *p*-Cresol = 1 : 1	34·7	31·75	28·7	25·5	22·1	18·6	14·9
m- + *p*-Cresol = 1 : 2	34·3	31·2	28·0	24·6	20·9	17·1	13·0
o-+*m*- + *p*-Cresol = 1 : 1 : 1	34·9	32·1	29·1	26·1	23·0	19·9	16·6

With regard to the change produced in the freezing point of phenol by the addition of a mixture of *m*-cresol and *p*-cresol, the table shows that the freezing point falls continuously as the proportion of the para-isomeride in the mixed cresol increases. The observed freezing points are, however, lower than those calculated from the separate effects produced by *m*-cresol and *p*-cresol on the basis of the simple mixture rule. For mixtures which contain a fixed proportion of phenol (60 to 80 per cent.), the variation of the freezing point with the composition of the admixed cresol is of such magnitude that the freezing point of such mixtures may be conveniently utilised in the estimation of *m*-cresol and *p*-cresol in their mixtures and in the evaluation of commercial "meta-cresol."

The change in the freezing point of phenol which is produced by the addition of a mixture of *o*-, *m*-, and *p*-cresol in equal proportions is slightly greater than that produced by the same quantity of *o*-cresol. The effect produced by *o*-cresol is within very narrow limits the same as that produced by a mixture of *m*-cresol and *p*-cresol in the proportion 2 : 1.

Lowering of the Freezing Point of o-*Cresol on the Addition of Phenol,* m-*Cresol, and* p-*Cresol.*

The weight percentage freezing-point curves show that equal quantities of phenol, *m*-cresol, and *p*-cresol lower the freezing point of *o*-cresol to different extents. The largest depression is produced by *p*-cresol, but the influence of *m*-cresol is not very different. On the other hand, the depression produced by the same weight of phenol is very much smaller, and this difference is probably due to the greater tendency of phenol to crystallise out with the *o*-cresol in the form of solid solutions. Table VIII affords a comparison of the freezing points of mixtures which contain equal weights of phenol, *m*-cresol, and *p*-cresol respectively; the numbers have been obtained by extrapolation from the corresponding curves.

TABLE VIII.

	Weight per cent. of solute.		
Nature of solute.	10 per cent.	20 per cent.	30 per cent.
Phenol	27·6°	24·95°	22·6°
m-Cresol	25·8	20·8	15·4
p-Cresol	25·2	19·6	13·2

Lowering of the Freezing Point of m-*Cresol on the Addition of Phenol,* o-*Cresol, and* p-*Cresol.*

The three curves which represent the depression of the freezing point of *m*-cresol on the addition of phenol, *o*-cresol, and *p*-cresol are characterised by their relatively short extension In the case where phenol is added, the limit is reached when the mixture contains less than 5 per cent. of phenol. In consequence of the small amount of pure *m*-cresol at our disposal and of the difficulty in measuring the freezing points with the requisite accuracy, these curves have not been examined in any detail. Although, therefore, further observations are required in order to determine the relative slopes of the curves, it seems probable that the freezing point of *m*-cresol is depressed to a greater extent by *p*-cresol than by the same quantity of *o*-cresol.

Lowering of the Freezing Point of p-*Cresol on the Addition of Phenol,* o-*Cresol, and* m-*Cresol.*

The behaviour of *p*-cresol as solvent is of particular interest by reason of the fact that its freezing point is depressed to almost exactly the same extent by equal weights of either phenol, *o*-cresol, or *m*-cresol. In this respect, *p*-cresol differs notably from phenol and *o*-cresol. The three freezing-point curves are, moreover, of wide range, the shortest extending to a point at which the temperature is about 26° below the freezing point of pure *p*-cresol. Since the weight percentage freezing-point curves are approximately identical, it follows that the freezing point of a mixture containing an excess of *p*-cresol affords a direct measure of the proportion of *p*-cresol in the mixture.

Summary and Discussion.

The freezing-point relations which have been described in the preceding pages show that there is considerable diversity in the behaviour of the several binary combinations when the liquid mixtures are allowed to crystallise.

In the case of binary mixtures which contain phenol in excess, the behaviour of the three cresols suggests that the tendency to crystallise out with the phenol increases markedly in the order *p*-cresol, *o*-cresol, *m*-cresol. With *p*-cresol as solvent, there is, on the other hand, very little difference in the behaviour of the three solutes phenol, *o*-cresol, and *m*-cresol, and although the experiments do not afford any quantitative information, it seems prob-

able that solid solution formation is very limited when mixtures containing an excess of *p*-cresol are allowed to crystallise. The position of *o*-cresol as solvent is intermediate, in that *m*-cresol and *p*-cresol as solutes show only a limited tendency to crystallise out with the *o*-cresol, whilst phenol separates out with the *o*-cresol in considerable quantities.

The fact that five out of the six binary systems afford evidence of the formation of definite compounds is rather remarkable in view of the close chemical similarity of the components. According to results obtained by Kendall and his co-workers (compare *J. Amer. Chem. Soc.*, 1917, **39**, 2303, and previous papers) in the investigation of the formation of additive compounds of various types of organic substances, it would appear that the formation of such compounds is in large measure determined by the difference in the basic or acid character of the components. The greater this difference, the greater the tendency to form additive compounds and the more stable the compounds which are formed. In the group of substances which we have examined, the differences in question are extremely small, and the relations disclosed by the freezing-point diagrams are consequently not in accord with what would have been anticipated on the basis of the views advocated by Kendall.

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LXXXV.—*The Estimation of Phenol and the Three Isomeric Cresols in Mixtures of these Substances.*

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IN the preceding paper, the authors have described the freezing-point diagrams for the six possible pairs of substances which correspond with the quaternary system phenol, *o*-cresol, *m*-cresol, and *p*-cresol. The relations exhibited by the diagrams suggest that the determination of the freezing point may prove to be of considerable value in the analysis of mixtures of these substances.

The value of the freezing-point measurement has long been recognised in connexion with the grading of commercial carbolic acids. It forms the basis of the widely used empirical method

described by Lowe for the standardisation and specification of coal-tar carbolics, and this method may, in fact, be used for the approximate estimation of phenol in commercial products which contain a sufficiently large proportion of phenol.

In recent years, the question of the estimation of phenol in tar acids has received considerable attention. Methods depending on freezing-point observations have been described by Weiss (*J. Franklin Inst.*, 1912, 683; compare also *J. Ind. Eng. Chem.*, 1917, **9**, 569) and by Masse and Leroux (*Compt. rend.*, 1916, **163**, 361), and a distinct advance in the application of the freezing-point method to the estimation of phenol in commercial carbolic and cresylic acids has been made by Fox and Barker (*J. Soc. Chem. Ind.*, 1917, **36**, 842; compare also *ibid.*, 1918, **37**, 265), whose method involves the production by distillation of a mixture in which the phenol is associated only with *o*-cresol

In attempting to determine completely the composition of mixtures containing phenol and the three cresols, we are concerned with a problem which is much wider in scope than that presented by the estimation of the phenol content. The four substances concerned give rise to six groups of binary mixtures, four groups of ternary mixtures, and the quaternary mixture in which all four are present. Theoretically, these various groups are of equal interest and importance, but a distinction can readily be made when the practice of the tar industry is considered. The separation of the homologues is based on differences in boiling point, and fractional distillation tends to eliminate the constituents in the order of their respective boiling points. For the four substances with which we are concerned, the approximate boiling points are: phenol 182°, *o*-cresol 192°, *m*-cresol 202°, *p*-cresol 202°. According to these data, it is evident that a binary mixture such as phenol and *m*-cresol, or a ternary mixture such as phenol, *o*-cresol, and *p*-cresol, will never be met with in works practice, and in this way it is possible to reduce the eleven possible groups of mixtures down to four which are of practical importance. These consist of the two binary series of mixtures with phenol and *o*-cresol, or *m*-cresol and *p*-cresol as components, the ternary series containing *o*-cresol, *m*-cresol, and *p*-cresol, and the quaternary series.

In reference to the application of physical methods in the analysis of liquid mixtures, it may be noted that binary mixtures present little difficulty. In the case of ternary mixtures, physical data are much more difficult to interpret, but under certain conditions it is possible to arrive at the composition of such mixtures without resort to chemical analysis. The application of chemical methods of separation would seem to be almost a necessity when

mixtures of greater complexity have to be dealt with. In the case of the four substances with which we are immediately concerned, the chemical properties are so similar that it has not yet been possible to devise a chemical method which is applicable to the general case of the quaternary mixture, and for this reason the attempt to solve the problem by the application of physical methods is of particular interest.

Before proceeding to describe the methods which we have devised for the analysis of the four groups of mixtures referred to above, it will be convenient to tabulate the values of certain physical properties.

TABLE I.

Property.	Phenol.	*o*-Cresol.	*m*-Cresol.	*p*-Cresol.
Density D_4^{25}	1·0710	1·0415	1·0295	1·0295
Freezing point.....	41·0°	30·45°	10·0°	34·15°
Boiling point (760 mm.)	182·2°	191·8°	202·1°	202·5°
Refractive index N_D (40°) ...	—	1·53719	1·53322	1·53187
Viscosity η (25°)	0·0883	0·0762	0·1240	0·1413
Solubility in water (20°), per cent.	8·5	2·8	2·3	2·0
Ionisation constant $K \cdot 10^{10}$ (25°)	1·15	0·63	0·98	0·67

The densities and freezing points given in the table are our own values, which in some cases differ appreciably from numbers recorded in the literature. For instance, the freezing point of *m*-cresol is about 6° higher than the values previously given. The boiling points and refractive indices are taken from Fox and Barker's paper (*loc. cit.*), the viscosities are values interpolated from Bramley's measurements (T., 1916, **109**, 434), the solubilities are those recorded by Sidgwick, Spurrell, and Davies (T., 1915, **107**, 1202), and the ionisation constants those given by Boyd (T., 1915, **107**, 1538). The differences shown by the cresols are not very large, but in certain cases they are sufficient to afford preliminary information of considerable value.

In proceeding to consider the four technically important groups of mixtures, it will be convenient to deal in the first place with the binary mixtures.

I. *Analysis of Mixtures of Phenol and o-Cresol.*

The densities of phenol and *o*-cresol are sufficiently different to permit of the density being used in the evaluation of mixtures of these substances. Although admixture is accompanied by a slight contraction, which amounts to about 0·033 per cent. in the case of the 50 per cent. mixture, the composition of any mixture may be calculated from its density by application of the simple mix-

ture rule. On account of the divergent values which are recorded in the literature for the density of *o*-cresol, it does not at present seem possible, however, to recommend the density for this purpose except as a means of providing preliminary information. In the circumstances, more satisfactory results would seem to be obtained by the freezing-point method.

By inspection of the freezing-point curves for mixtures of phenol and *o*-cresol, it will be observed that the slope of the phenol branch is much steeper than that of the *o*-cresol branch, and also that the change in freezing point is very small for a certain range of mixtures. The greater slope of the phenol curve signifies a greater sensitiveness of the freezing point to change in composition when the mixture contains an excess of phenol, and the flat portion indicates that the composition of mixtures which contain more than about 30 and less than about 70 per cent. of *o*-cresol cannot be estimated directly by the freezing-point method.

Having regard to these facts, the examination of an unknown mixture, X, may advantageously begin with the measurement of its density. If the mixture contains phenol or *o*-cresol in considerable excess ($D_4^{25} > 1{\cdot}061$ or $< 1{\cdot}050$), the composition may be deduced directly from the freezing point of X, the phenol branch being used for the mixtures of higher density and the *o*-cresol branch for those falling within the lower range. If the density lies between the above limits, X should be mixed with a known proportion of standard phenol (m. p. 40·5°), so as to raise the density of the resulting mixture, Y, above 1·061. The freezing point of Y is then measured. Assuming that a parts of X are mixed with $100-a$ parts of phenol, and that this mixture, Y, contains, according to the freezing-point measurement, y per cent. of phenol, then the percentage of phenol in X is given by the equation $x=(y-100+a)100/a$.

In table II we give the freezing points of mixtures rich in phenol or in *o*-cresol from which the composition of any such mixture may be derived.

TABLE II.

Weight per cent. phenol.....	100	95	90	85	80	75	70
Freezing point	40·5°	37·9°	35·2°	32·4°	29·5°	26·5°	23·4°
Weight per cent. *o*-cresol	100	95	90	85	80	75	70
Freezing point	30·45°	29·0°	27·6°	26·25°	24·95°	23·7°	22·6°

Example.—$X=48{\cdot}0$ per cent. phenol, 52·0 per cent. *o*-cresol. $Y=40{\cdot}4$ per cent. $X+59{\cdot}6$ per cent. phenol, freezing point 28·8°. Per cent. phenol in $Y=78{\cdot}7$, whence per cent. phenol in $X=47{\cdot}3$.

II. *Analysis of Mixtures of* m-*Cresol and* p-*Cresol.*

By reference to table I, it is evident that the differences between the physical properties of liquid *m*- and *p*-cresol are very small. Greater differences are found in their chemical behaviour, and Raschig (*Zeitsch. angew. Chem.*, 1900, **14**, 759) has described a nitration method which is said to afford a means of estimating *m*-cresol in mixtures which contain all three cresols The claim that the yield of trinitro-*m*-cresol is independent of the proportions of *o*-, *m*-, and *p*-cresol in the mixture is not supported by the results which we have obtained.

A further chemical method, described by Ditz and Cedivoda (*Zeitsch. angew. Chem.*, 1899, **13**, 873, 879), is based on the greater bromine absorbing capacity of *m*-cresol as compared with that of *o*-cresol and *p*-cresol, but it does not seem to have been established that trustworthy results can be obtained in this way.

If the freezing-point diagram for mixtures of *m*-cresol and *p*-cresol (Fig. 4 of preceding paper) is examined, it will be observed that the *p*-cresol curve extends over a considerable range, and that the curve is such that small changes in composition have a considerable influence on the freezing point. The *p*-cresol curve is accordingly well adapted for use in the estimation of *p*-cresol in mixtures of *m*- and *p*-cresol. In applying the freezing-point method, the mixture *X* may advantageously be mixed with a known proportion of pure *p*-cresol and the freezing point of the resulting mixture, *Y*, determined. The ratio *X* : *p*-cresol = 1 : 2 will be found most generally convenient. From the freezing point, the percentage of *p*-cresol may then be read off from the curve which corresponds with the numbers in table III, and the percentage of *p*-cresol in *X* calculated as previously described.

Table III.

Freezing Points of p-*Cresol in Admixture with* o-*Cresol,* m-*Cresol, or Phenol.*

p-Cresol, per cent. ...	100	95	90	85	80	75	70	65
Freezing point.....	34·15°	30·7°	27·2°	23·6°	20·0°	16·3°	12·3°	7·8°

If the freezing point of mixture *Y* is higher than about 25°, *X* may be mixed with a smaller proportion of *p*-cresol, and the freezing-point measurement repeated.

An alternative freezing-point method for the estimation of the proportions of *m*-cresol and *p*-cresol in a mixture of the two has already been referred to in the preceding paper. In the applica-

tion of this method, the mixture X should be mixed with standard phenol to give a ternary mixture which contains 60 to 70 per cent. of phenol. The freezing-point of this phenol–cresol mixture is determined, and since the temperature varies considerably when the percentage of phenol in the mixture is kept constant and the ratio of *m*-cresol to *p*-cresol in the admixed cresol is altered, it follows that the composition of the mixture X may be deduced from the observed freezing point. Table IV gives the freezing points of mixtures containing 60, 65, and 70 per cent. of phenol respectively, the composition of the admixed cresol being indicated by the horizontal series of figures, ranging from 0 to 100 per cent. of *m*-cresol.

TABLE IV.

Freezing Points of Mixtures of Phenol, m-*Cresol, and* p-*Cresol.*

Per cent. phenol in ternary mixture.	Per cent. *m*-cresol in mixture of *m*- and *p*-cresol.										
	0	10	20	30	40	50	60	70	80	90	100
60	9·5°	10·5°	11·6°	12·7°	13·8°	15·0°	16·4°	17·8°	19·3°	21·0°	23·6°
65	14·4	15·1	15·9	16·8	17·8	18·8	19·9	21·0	22·2	23·5	25·0
70	19·0	19·5	20·1	20·7	21·4	22·1	22·9	23·8	24·8	26·0	27·3

Although this method is not so sensitive as the method of analysis which is based on the use of the *p*-cresol freezing-point curve, it has been found to be quite trustworthy.

Example.—X = mixture of *m*-cresol and *p*-cresol.

First Method.—$Y = 30{\cdot}6$ per cent. $X + 69{\cdot}4$ per cent. *p*-cresol, freezing point 16·5°, from which per cent. *p*-cresol in $Y = 75{\cdot}3$ and in $X = 19{\cdot}3$.

$Y' = 37{\cdot}8$ per cent. $X + 62{\cdot}2$ per cent. *p*-cresol, freezing point 12·3°, from which per cent. *p*-cresol in $Y' = 70{\cdot}0$ and in $X = 20{\cdot}6$.

Second Method.—$Z = 33{\cdot}4$ per cent. $X + 66{\cdot}6$ per cent. phenol, freeing point 23·35°, from which, by reference to curves constructed from the numbers in table IV (see above) and the data contained in table VII of the preceding paper, per cent. *p*-cresol in $X = 19$.

III. *Analysis of Ternary Mixtures containing* o-*Cresol,* m-*Cresol, and* p-*Cresol.*

Since *m*-cresol and *p*-cresol have the same density, which is appreciably less than the density of *o*-cresol, and the volume changes which occur on mixing are very small, the measurement

of the density affords a rough estimate of the proportion of *o*-cresol in the ternary mixture under examination. Not much information can be obtained from the investigation of other physical properties of a ternary liquid mixture, but the nitration and bromination methods will afford some indication of the proportion of *m*-cresol.

A ternary mixture of the cresols may, however, be completely analysed, without resort to chemical methods, by means of suitable freezing-point measurements. The method depends on the fact that equal weights of *o*-cresol and *m*-cresol depress the freezing point of *p*-cresol to the same extent, and on the further fact that equal weights of *m*-cresol and *p*-cresol depress the freezing point of *o*-cresol to nearly the same extent. In the application of the method, the unknown mixture *X* is mixed with a known quantity of pure *p*-cresol, giving a mixture, *Y*, the freezing point of which is determined. From this, the percentage of *p*-cresol in *Y*, and hence in *X*, can be obtained from the freezing-point curve corresponding with the numbers already given in table III.

Similarly, *X* is mixed with a known proportion of pure *o*-cresol, giving a mixture, *Z*, the freezing point of which is also measured. From this, the percentage of *o*-cresol in *Z*, and hence in *X*, may be derived from the freezing points recorded in table V. These temperatures correspond with a freezing-point curve which lies between the curves representing the changes produced in the freezing point of *o*-cresol on the addition of *m*-cresol and *p*-cresol respectively.

TABLE V.

Freezing Points of o-*Cresol in Admixture with* m- *and* p-*Cresol.*

o-Cresol, per cent. ...	100	95	90	85	80	75	70	65
Freezing point.....	30·45°	28·05°	25·6°	23·1°	20·4°	17·5°	14·4°	11·0°

The proportions of *p*-cresol and *o*-cresol most suitable for the production of the mixtures *Y* and *Z* are indicated, if necessary, by preliminary freezing-point observations on mixtures containing one part of *X* and two parts of *p*-cresol and *o*-cresol respectively.

Example.—*X* = 42·5 per cent. *o*-cresol, 46·0 per cent. *m*-cresol, 11·5 per cent. *p*-cresol.

(*a*) Estimation of *p*-cresol.

Y = 23·5 per cent. *X* + 76·5 per cent. *p*-cresol, freezing point 19·5°, whence per cent. *p*-cresol in *Y* = 79·3 and in *X* = 11·9.

Y' = 29·4 per cent. *X* + 70·6 per cent. *p*-cresol, freezing point 15·1°, whence per cent. *p*-cresol in *Y'* = 73·5 and in *X* = 10·0.

(*b*) Estimation of *o*-cresol.

$Z = 26{\cdot}1$ per cent. $X + 73{\cdot}9$ per cent. *o*-cresol, freezing point 23·0°, whence per cent. *o*-cresol in $Z = 84{\cdot}8$ and in $X = 41{\cdot}8$.

$Z' = 42{\cdot}3$ per cent. $X + 57{\cdot}7$ per cent. *o*-cresol, freezing point 17·6, whence per cent. *o*-cresol in $Z' = 75{\cdot}2$ and in $X = 41{\cdot}4$.

Taking the mean values found for *p*-cresol and *o*-cresol, the freezing-point method of analysis gives $X = 41{\cdot}6$ per cent. *o*-cresol, 47·4 per cent. *m*-cresol, 11·0 per cent. *p*-cresol.

IV. *Analysis of Quaternary Mixtures containing Phenol,* o-*Cresol,* m-*Cresol, and* p-*Cresol.*

The determination of the composition of a quaternary mixture involves the assignment of definite values to each of three independent variables, and in these circumstances the physical properties of the liquid mixtures afford comparatively little information with regard to the proportions of the components except in certain special cases. At the same time, an approximate idea of the nature of the mixture may be obtained from the density, the freezing point, and the behaviour of the liquid when it is subjected to slow fractional distillation with a suitable still-head. In connexion with the behaviour on distillation, attention may be directed to the tables recording the observations made by Fox and Barker (*loc. cit.*). The significance of the density and the freezing point will be apparent from table I and the freezing-point relations which have already been described.

In regard to chemical methods, the nitration and bromination processes are of little use when we are dealing with quaternary mixtures. On the other hand, a method described by Skirrow (*J. Ind. Eng. Chem.*, 1917, **9**, 1102), which involves the measurement of the rate of oxidation of the phenols by permanganate in sulphuric acid solution, seems to afford an approximate measure of the percentage of phenol present in quaternary mixtures, although the nature of the admixed cresol has a very appreciable influence on the velocity of the oxidation process.

The information to be derived from the direct application of the freezing-point method to quaternary mixtures is strictly limited, in that only one of the three independent variables, in terms of which the composition of such a mixture may be expressed, can be determined in this way. This variable is the proportion of *p*-cresol, which may be estimated according to the method already described in sections II and III. The applicability of this method to the quaternary mixture depends on the fact that the freezing point of *p*-cresol is lowered to the same extent by equal quantities of phenol, *o*-cresol, and *m*-cresol.

Examples:

(1) $X = 19{\cdot}5$ per cent. phenol, $20{\cdot}0$ per cent. *o*-cresol, $36{\cdot}4$ per cent. *m*-cresol, $24{\cdot}1$ per cent. *p*-cresol.

$Y = 33{\cdot}2$ per cent. $X + 66{\cdot}8$ per cent. *p*-cresol, freezing point $16{\cdot}15°$, from which per cent. *p*-cresol in $Y = 74{\cdot}8$, and hence in $X = 24{\cdot}0$.

(2) $X = 10{\cdot}0$ per cent. phenol, $20{\cdot}0$ per cent. *o*-cresol, $56{\cdot}0$ per cent. *m*-cresol, $14{\cdot}0$ per cent. *p*-cresol.

$Y = 25{\cdot}4$ per cent. $X + 74{\cdot}6$ per cent. *p*-cresol, freezing point $18{\cdot}9°$, from which per cent. *p*-cresol in $Y = 78{\cdot}5$, and hence in $X = 15{\cdot}3$.

Although the direct application of the freezing-point method to quaternary mixtures is thus limited to the estimation of *p*-cresol, it appears to be possible to analyse such mixtures completely by physical methods if the mixtures are subjected to a preliminary fractionation. In carrying out this process, the quaternary mixture X is mixed with about half its weight of *o*-cresol, following the device recommended by Fox and Barker (*loc. cit.*) in connexion with the estimation of phenol. This mixture, X', is then submitted to slow fractional distillation with a still-head of the Raschig type, and by this means X' is separated into two fractions, one of which (A) consists of a mixture of phenol and *o*-cresol and the other (B) of a mixture of *o*-cresol, *m*-cresol, and *p*-cresol. The fractions A and B are then analysed by application of the freezing-point methods, which have been already described in sections I and III.

As yet it has not been possible, in view of the urgency of other work, to test this method in any detail, but the preliminary observations which have been made seem to show that satisfactory results for quaternary mixtures containing phenol and the three cresols may be obtained in this way.

In reference to the application of the freezing-point methods which have been described, it should be explained that great care is needed to ensure that the materials used are free from water. The tables of data and the corresponding curves may only be applied directly to the interpretation of freezing points determined by other observers when the standard samples of phenol and of the cresols have freezing points which are identical with those of the samples used by us. With regard to these samples, it is probable that pure anhydrous phenol melts at about 41°, and our use of phenol melting at $40{\cdot}5°$ was determined by the fact that a substance of this melting point could readily be prepared from ordinary samples of phenol. The melting point of *o*-cresol ($30{\cdot}45°$)

is slightly higher than that recorded in the literature, but we have found that *o*-cresol of this quality may readily be obtained from the commercial product. The *m*-cresol (m. p. 10·0°) was probably not quite pure, although this temperature is much higher than that previously recorded. With regard to the *p*-cresol, it may be mentioned that a substance of this melting point (34·15°) was obtained from two different samples of synthetic material. This temperature is lower than that recorded by certain observers, but agrees fairly closely with the value of 33·8° given by Sidgwick, Spurrell, and Davies (*loc. cit.*), and by Bramley (*loc. cit.*). The use of standard materials differing but slightly in freezing point from those employed by us does not prevent the use of the tables of figures recorded in the paper, for experience has shown that it is possible to make suitable allowance for such differences if these are small. In actual practice, it will no doubt be found preferable to draw up corresponding tables which are directly applicable to the available standard substances and to such modified conditions of working as may seem advisable. These are matters of detail which do not affect the general methods of procedure which have been described.

Summary.

An account is given of the application of physical methods in the analysis of the technically important series of mixtures: (*a*) phenol and *o*-cresol, (*b*) *m*-cresol and *p*-cresol; (*c*) *o*-cresol, *m*-cresol, and *p*-cresol, (*d*) phenol, *o*-cresol, *m*-cresol, and *p*-cresol. It is shown that freezing-point measurements may be utilised for the complete determination of the composition of the binary and ternary mixtures. In the case of the quaternary mixture, the application of the freezing-point methods is preceded by a fractionation process, in which the quaternary is mixed with a known quantity of *o*-cresol and separated into two fractions containing (1) phenol and *o*-cresol, (2) *o*-cresol, *m*-cresol, and *p*-cresol.

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LXXXVI.—*The Oxidation and Ignition of Coal.*

By Richard Vernon Wheeler.

This paper contains an abbreviated account of work that has been carried out intermittently during the past nine years, at the outset for the Mining Association of Great Britain (British Coal Dust Experiments Committee) and during later years at the Home Office Experimental Station.

The earlier work (to which Mr. M. J. Burgess contributed the largest share during 1909—1911) was withheld from publication from the desire eventually to present a complete study of the cause of the spontaneous combustion of coal. The main results were, however, communicated privately to individuals particularly interested in the subject, and the conclusions reached were summarised in evidence before the Departmental Committee on Spontaneous Combustion in Coal Mines in 1913 (Minutes of Evidence, first to seventh days).

At a later date, the Doncaster Coal Owners founded a laboratory, under the direction of Dr. J. S. Haldane, to specialise in the study of the spontaneous combustion of coal, and a series of papers has emanated from that laboratory (*Trans. Inst. Min. Eng.*, 1914, **46**, 563; 1915, **48**, 503; **49**, 35; 1916, **51**, 493; **52**, 338; 1918, **54**, 197). This series of papers renders the publication of the details of much of the work herein summarised unnecessary, for although the experiments were carried out in a different manner they have little to add to the results obtained at Doncaster.

The first method of experiment adopted was to circulate air or oxygen in a closed system through a column of powdered, freshly-won coal, heated in a constant-temperature oven, and to measure the rate of disappearance of oxygen by the rate of diminution of pressure in the system. Samples of the gases were taken at intervals throughout an experiment (some of which were continuous during several weeks) by means of by-passed sampling tubes so arranged that the removal of the sample did not alter the pressure in the circulation system.

It may be said at once that the results obtained by these means did not afford as much information as was desired or expected, and other methods of experiment, shortly to be described, were ultimately adopted. It was found, in conformity with the results of earlier and recent investigators*:

* A review of the more important work on spontaneous combustion is contained in Professor W. A. Bone's recent book, "Coal and its Scientific Uses" (London, 1918), pp. 149—163.

(1) That the absorption of oxygen by newly-won bituminous coal is initially very rapid, even at ordinary atmospheric temperatures, but that this rapid absorption soon gives place to a slow but long-continued absorption.

(2) That the initial rapid absorption of oxygen at low temperatures is not accompanied, so far as could be ascertained, by the formation of water or the oxides of carbon, but that during the second, slow phase of the absorption these products of oxidation of the coal substance make their appearance, the amounts increasing with the temperature of the coal.

(3) That the ratio CO_2/CO in the products of combustion remained appreciably constant for a given coal at a given temperature throughout the period of long-continued slow absorption of oxygen, the ratio decreasing with increased temperature.

These facts did not, however, bring one much nearer to an explanation of the mechanism of the reaction between oxygen and coal that results in "spontaneous combustion," and they gave no indication of the reason why one coal is more liable to self-heat than is another.

The Oxidation of Coal.

It has already been stated that during the rapid absorption of oxygen that takes place when newly-won coal is exposed to air at atmospheric temperature, the simultaneous formation of carbon dioxide or carbon monoxide could not be detected, although both these gases make their appearance subsequently. It had been noticed, however, that the "occluded gases" that can be removed from any sample of coal by exhaustion at 100° contain a high proportion of the oxides of carbon if the coal has been previously "weathered," either naturally or artificially, thus differing from the gases withdrawn from newly-won coal, which consist mainly of methane and the higher members of the paraffin series of hydrocarbons (see Burgess and Wheeler, T., 1914, **105**, 131).

From this it was thought that there might be a reaction between oxygen and some part of the coal substance analogous to that between carbon and oxygen, investigated by Rhead and Wheeler (T., 1913, **103**, 461), which is characterised by the fixation of oxygen, the presumption being that an unstable compound of carbon and oxygen is formed.

Experiments were therefore made with the intention of examining more closely the composition and occurrence of the occluded gases in artificially weathered coal. Freshly-won coal * from that

* The coal as soon as it was hewn was packed tightly in a box which was hermetically sealed and dispatched the same day to the laboratory.

portion of the Thick Coal Seam at Hamstead Colliery, termed "Slips," was roughly crushed and thoroughly exhausted at 100° to free it from naturally occluded gases, 230 grams being taken for the experiment. Undried air was then slowly drawn through the coal at a temperature of 15° during forty-eight hours, and, after the apparatus had been rapidly exhausted by means of a Geryk oil-pump, any gases contained in the coal were extracted by a Sprengel mercury pump and collected. The results were:

	Analysis, per cent.			
	CO_2.	O_2.	CO.	N_2.
Gases removed at 15°	11·18	4·2	nil	84·0
Gases removed between 15° and 100° ...	43·5	20·6	6·9	29·0

A total volume of 31·5 c.c. of gases (measured at 0° and 760 mm.) was removed from the coal.

This experiment gives a definite indication that, whereas some oxygen is occluded by coal at 15° and can be removed therefrom as such by physical means, the major portion of the oxygen retained by the coal only makes its appearance as oxides of carbon when the temperature of the coal is raised.

The same weight (230 grams) of newly-won coal, roughly crushed, from the "Brazils" portion of the Thick Coal Seam, Hamstead Colliery, was treated in a similar manner: the naturally occluded gases having been removed, air was aspirated through the coal during twenty-four hours; most of the air in the apparatus having been removed at the ordinary temperature by several strokes of a Geryk oil-pump, the temperature of the coal was raised to 100° and the gases were collected, no separation being made between the gases removed at 15° and at 100°, as with the "Slips" coal. This series of operations was performed several times with the variations in treatment described in the table on p. 948.

It will be seen that, under similar treatment, the "Brazils" coal yielded less gases than did the same weight of the "Slips" coal. A more important observation is the marked increase in the quantity of gas retained by the coal when the air passed over it was dried by calcium chloride. To confirm this, a series of experiments was made in a slightly different manner, using 100 grams of "Brazils" coal that had been crushed so as to pass through a 10×10 and remain on a 30×30 mesh sieve, and from which the naturally occluded gases had been removed.

After treatment of the coal with air (either saturated with water vapour at 15° or dried by passing through calcium chloride towers) during six hours at different temperatures, the apparatus

Treatment.	Volume of gases removed up to 100°. c.c. at 0° and 760 mm.	Analysis, per cent. CO_2.	O_2.	CO.	N_2.
A. Undried air aspirated through the coal during 24 hours at 15°	18·9	11·9	5·1	2·3	80·7
B. Air dried by calcium chloride aspirated through the coal during 24 hours at 15°	40·3	15·5	8·7	3·2	72·6
C. As with B	45·0	25·5	3·7	2·3	68·5
D. As with A	24·0	16·8	13·4	1·3	68·5
E. Air saturated with water-vapour at 15° aspirated through the coal during 24 hours at 15°...	22·0	25·8	12·6	3·4	58·2
F. Air saturated with water-vapour at 15° aspirated through the coal during 24 hours at 50°.....	23·4	49·7	8·8	5·3	36·2
G. Air dried by calcium chloride aspirated through the coal during 24 hours at 50°	32·5	29·7	7·3	5·5	57·5

was thoroughly exhausted at the ordinary temperature by a Sprengel mercury pump, and only those gases collected that were withdrawn from the coal when its temperature was raised from 15° to 100°. The results were:

Treatment.	Volume of gases removed between 15° and 100°. c.c. at 0° and 760 mm.	Analysis. CO_2.	O_2.	CO.	N_2.	Ratio. CO_2/CO
A. Moist air at 15°.....	17·7	28·0	2·8	2·2	67·0	12·7
B. Dried air at 15°.....	30·8	15·4	nil	1·8	82·8	8·6
C. Moist air at 50°	18·7	42·0	4·7	3·9	49·4	10·8
D. Dried air at 50°	27·0	12·8	1·5	1·7	84·0	7·5
E. Moist air at 100°	6·8	77·0	1·8	13·2	8·0	5·8
F. Dried air at 100°	8·9	31·3	0·2	8·3	60·2	3·8

These results, apart from the difference observable between the effects of moist and dried air (a matter requiring further study), bear a striking resemblance to the result of passing air over carbon at low temperatures, and a similar explanation of them can be offered, namely, that "the first step in the oxidation of coal is the formation of an addition compound, or complex, of oxygen with one or more of the substances present in coal."

This conclusion, founded on the results of experiments of a different character from those described in this paper, has been put

forward also by Porter and Ralston ("A Study of the Oxidation of Coal," United States Bureau of Mines, Technical Paper 65, 1914), from whose paper the foregoing quotation is made. Porter and Ralston continue: "This complex is unstable and decomposes readily—more readily with some coals than with others—setting free water, CO_2, and CO."

It should not be supposed that the similarity in the behaviour of oxygen towards both coal and carbon is indicative of the presence of "free" carbon in coal. Experimental evidence as to the existence of free carbon as a normal constituent of coal is difficult, if not impossible, to obtain. This matter has been discussed by Jones and Wheeler (T., 1916, **109**, 709), who have pointed out that none of the factors, singly or combined, involved in the formation of coal can have brought about the complete carbonisation of any portion of the substances from which it is formed. On the other hand, the existence in coal of substances the molecules of which are similar in type to the carbon molecule must be presumed. Dimroth and Kerkovius (*Annalen*, 1912, **399**, 120) have shown that the carbon molecule contains the fluorene grouping, whilst Pictet and Ramseyer (*Ber.*, 1911, **44**, 2486) have extracted hexahydrofluorene from Montrambert coal. Moreover, both carbon and coal yield benzenehexacarboxylic acid (mellitic acid) on oxidation, showing that in both there are molecules present the structure of which involves a six-carbon ring, each carbon atom of which is attached to an additional carbon atom.

In order to discover the exact nature of the compounds thus presumed responsible for the "first step in the oxidation of coal," a more intimate knowledge is required than is possessed at present of the chemical constitution of the coal substance. A solution of the problem of the spontaneous combustion of coal is, in fact, largely dependent on the success of the endeavours that are being made to resolve the coal conglomerate into its component parts. No doubt suitable "oxidation" experiments will contribute towards this end, inasmuch as they should afford information regarding the chemical characteristics of different parts of the coal conglomerate.

The Ignition of Coal.

The reaction between oxygen and coal that results in the "fixation" of the oxygen is accompanied by a heating effect, so that if pains are taken to prevent the dissipation of heat, the temperature of the coal rises. An increase in the temperature of the coal increases its rate of reaction with oxygen; if the rate of reaction is productive of more heat per unit of time than is sufficient to

counterbalance loss incidental to the physical conditions obtaining, it follows that eventually the coal will ignite.

Thus it is that spontaneous fires may occur in coal, in the mine or on the surface; and thus it is that several factors other than the chemical constitution of the coal have to be considered when attempting to guard against such fires. On the chemical constitution of the coal the rate of its reaction with oxygen at a given temperature mainly depends, but its state of division, permeability, and physical condition generally, also affect the rate of reaction; whilst the rate of dissipation of heat is governed by such factors as the amount of ventilation and the thermal conductivity of the coal itself and of its surroundings.

When determining the relative ignition-temperatures of different coals, it is not easy to decide what criterion of "ignition" should be employed. If one adopts the generally accepted definition of "ignition-temperature" as applied to gaseous mixtures (that is, that temperature at which self-heating of the mixture begins to take place), the ignition-temperature of most coals is the normal atmospheric temperature. A distinction between one coal and another could no doubt be made by determining the time taken for this self-heating from atmospheric temperature to result in flame under standard conditions.

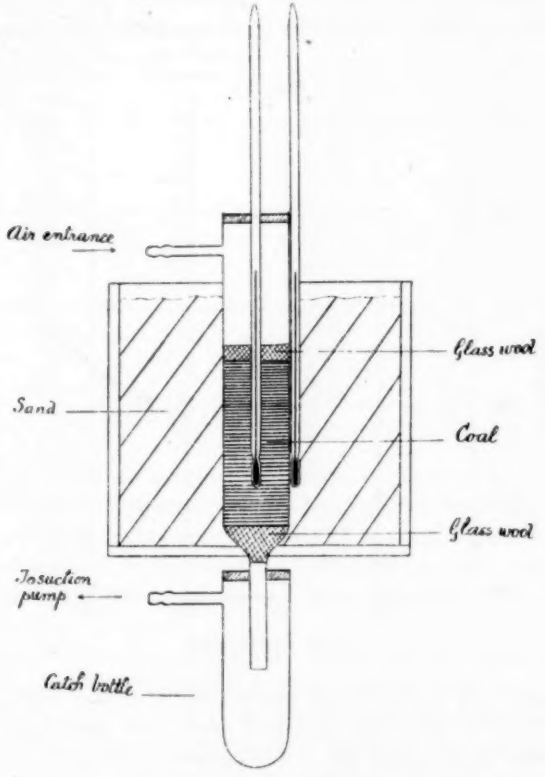
It may be of value also to know at what temperature a given coal must be heated in air, under specified conditions, in order that it shall burst into flame, and this temperature may perhaps be regarded as the "ignition-temperature," the preliminary self-heating (corresponding with the "pre-flame period" with gases) being ignored. Experimental difficulties, however, stand in the way both of determining accurately the moment when flame first appears in a mass of coal, and of ensuring that in comparative tests with different coals all the factors on which the appearance of actual flame depends are maintained constant.

From a practical as well as from a theoretical point of view, it is sufficient to know at what temperatures, under standard conditions, different coals begin to react with oxygen so rapidly that the ultimate appearance of flame is assured. If, for example, air is drawn at a constant speed through a column of powdered coal, the temperature of which is gradually raised by an external source of heat, eventually the temperature within the coal will begin to rise rapidly above that of the external source of heat. It is then only a matter of time, depending on the physical conditions of the test, before the coal will inflame.

In order to determine what relationship, if any, there is between the chemical composition of a coal and its ignition-temperature, a

number of coals were tested in the following manner. Forty grams of the powdered coal that had passed through a 150×150 and remained on a 240×240 mesh sieve were placed in a glass tube of the form shown diagrammatically in Fig. 1, making a column about 12 cm. long. This tube was fixed vertically in an electrically heated sand-bath, and a current of air (dried by passing through calcium chloride towers) drawn through it at a constant

FIG. 1.



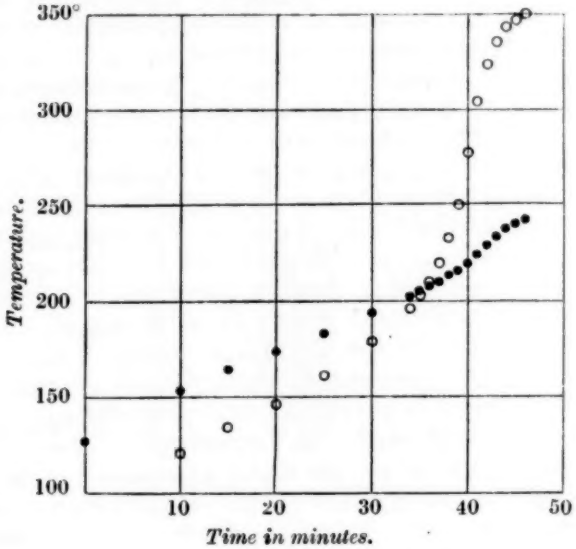
speed. The temperature of the sand-bath was then slowly raised, at a uniform rate, and simultaneous readings of two thermometers, the one embedded in the coal and the other in the sand, taken at frequent intervals of time.

In this manner, two time–temperature curves were obtained, the one showing the rate of rise of temperature of the sand-bath and the other the rate of rise of temperature of the coal. At a given temperature, depending on the coal employed, these two curves cut

one another. This temperature was taken to be the ignition-temperature of the coal relative to other coals tested in the same manner.

In Fig. 2, an example of the results obtained is given. Only the later portions of the two curves are shown; during the earlier stages of the heating (from atmospheric temperature) the curves run parallel to each other. It will be seen that the temperature at which the reaction-velocity became so rapid that the inflammation of the coal was imminent is clearly indicated at about 205°. It is evident also from the gradual approach of the two curves that the heat due to oxidation of the coal was sufficient, despite loss to

FIG. 2.



the outgoing air, to raise the temperature of the coal above that normally due to the heat received from the sand-bath when the reaction was proceeding at a temperature of 125°. The latter temperature might be regarded as the ignition-temperature of the coal (that is, the temperature at which self-heating began) under the conditions of the experiment. For comparative purposes, however, it was found preferable to record, as the relative ignition-temperature, the point at which the coal temperature curve and the sand-bath temperature curve cut one another, for this point is clearly defined. It is the temperature at which rapid self-heating begins, and is therefore in conformity with Nernst's definition of the ignition-temperature for gaseous mixtures.

In the table that follows are given the relative ignition-temperatures as thus determined for a number of bituminous coals. Full analyses of the coals, which are referred to under laboratory numbers, have been published in the Second Report of the Explosions in Mines Committee (H.M. Stationery Office, Cd. 6431 of Session 1912—1913).* The oxygen-contents only are reproduced here, for if reference be made to the full analyses it will be seen that no relationship exists between the ignition-temperatures now recorded and other analytical data.

Coal number.	Oxygen-content. (Per cent. on ash-free dry coal.)	Relative ignition temperature.	Coal number.	Oxygen-content. (Per cent. on ash-free dry coal.)	Relative ignition temperature.
213	11·1	165°	247	8·3	182°
210	11·1	165	240	8·1	180
218	11·1	167	216	8·0	183
248	10·6	177	224	7·6	192
251	10·5	176	226	7·4	188
234	10·3	176	200	7·3	185
207	9·9	177	205	7·0	192
246	9·9	179	239	6·7	195
208	9·9	179	215	6·6	206
211	9·5	178	230	6·4	200
235	9·2	178	214	5·6	210
231	8·8	183	203	5·4	200
201	8·8	187	217	5·1	217
206	8·7	186	232	4·9	195
241	8·6	183	227	4·7	220
225	8·5	185	228	3·9	200

It is clear from this table that the statement made by several investigators, that the most highly oxygenated fuels are those most liable to self-heat, a statement intended to distinguish between the different classes of fuels—lignitic, bituminous, and anthracitic—holds with remarkable closeness for coals of the same class (bituminous).

If it is correct to assume that the similarity in behaviour towards oxygen evinced by bituminous coal and carbon is due to the presence in the coal of groups of compounds the molecules of which have aromatic structures resembling those of the carbon molecule, it follows that the greater the proportion of such groups of compounds in a coal the greater will be the ability of that coal when newly-won to "attach" oxygen, and the higher will be its proportion of oxygen when "saturated."

The oxygen-contents given in the table must be regarded as those of the "saturated" coals; for the treatment to which the coals had been subjected—their pulverisation and sieving—involved the exposure of the fine dusts to air at 15° for a length of time sufficient

* A certain number of the analyses are recorded also in T., 1913, **103**, 1722.

to saturate them with oxygen at that temperature. Since the samples taken for the combustion analyses were accorded the same treatment as the samples tested for ignition-temperatures, the relationship between oxygen-content and ignition-temperature is not affected by this saturation with oxygen; but it is necessary to remember that some of the oxygen recorded as present in each coal must be in the form of the presumed complex.

It is not remarkable that a coal containing a high proportion of oxygenated compounds should show signs of rapid self-heating in an air-stream at a temperature lower than that required by a coal of less oxygen-content. What is known of the constitution of coal points to the major portion of the oxygenated compounds normally present being compounds arising from the degradation of the celluloses and compound celluloses of the cell-walls of the coal-plants. It is just these compounds of which the structures of the molecules approximate most closely in character to those of carbon, which therefore may presumably act like carbon in causing a loose attachment of oxygen. A coal rich in such compounds—oxygenated compounds—might therefore be expected to absorb oxygen readily and, *ipso facto*, to self-heat readily.

The term "self-heat" may, moreover, be seen to have its true significance so far as a highly oxygenated, "saturated," coal is concerned if one considers that the loosely combined oxygen may at a higher temperature desire a more permanent attachment—may, so to say, bite where previously it has only nibbled. If any reaction of this nature does indeed take place, an evolution of heat should be observed when a "saturated" coal is heated slowly in a vacuum or in an inert atmosphere. Hollings and Cobb (*J. Gas Lighting*, 1914, **126**, 917), in the course of their study of the thermal phenomena occurring during carbonisation, obtained several heating curves which show a marked exothermic reaction (in an atmosphere of nitrogen) between 150° and 250°. Hollings and Cobb at a later date (T., 1915, **107**, 1109) stated that they attached no importance to deflexions of their heating curves at temperatures lower than 200°, apparently because they considered it "hardly possible that between 150° C. and 250° C. there can be any exothermic reaction in an inert atmosphere" (*loc. cit.*, p. 920); but the deflexions shown in their earlier paper are too large to be ignored. It is significant that the range, 150° to 250°, over which the exothermic reaction with coal in a stream of nitrogen is manifest in Hollings and Cobb's experiments should correspond so closely with the range over which, with the series of coals tested in the present research, rapid self-heating occurs in a stream of air.

The lines upon which the researches are being continued are obvious. At their present stage, the following working hypothesis can be advanced: The reaction responsible for the "self-heating" of coal is mainly one of attachment of oxygen to molecules of high carbon-content. Subsidiary to this reaction, but playing an important part in determining the actual spontaneous ignition of coal, is a chemical interaction between the oxygen thus loosely held, by the carbon-like molecules, and other atoms in those molecules, or other portions of the coal conglomerate.

I wish to acknowledge the assistance of Mr. C. B. Platt during the experiments described under the heading "The Oxidation of Coal," and of Messrs. M. J. Burgess and T. F. E. Rhead during the experiments on the ignition of coal.

[*Received, October 12th,* 1918.]

LXXXVII.—*Studies in the Tetrahydronaphthalene Series.*

By Arthur G. Green and Frederick Maurice Rowe.

A. ar-*Tetrahydro-α-naphthylamine.*

ar-Tetrahydro-α-naphthylamine has been shown to possess many interesting peculiarities. It has the general properties of an aromatic amine, yet, whilst on the one hand it resembles aniline and its homologues (particularly *o*-2-xylidine) rather than α-naphthylamine (Bamberger, *Annalen*, 1890, **257**, 11), on the other it is similar to α-naphthylamine in the facility with which it reacts with diazonium salts, forming aminoazo-derivatives far more readily than does *o*-2-xylidine (Noelting and Forel, *Ber.*, 1885, **18**, 2682). Of further interest is the fact that azo-dyes derived from *ar*-tetrahydro-α-naphthylamine differ considerably in shade from similar azo-dyes derived from α-naphthylamine, and in this respect approximate to dyes derived from benzenoid amines (Bamberger, *Ber.*, 1887, **20**, 2915; Bamberger and Bordt, *ibid.*, 1889, **22**, 625; Morgan and Richards, *J. Soc. Chem. Ind.*, 1905, **24**, 652). In view of the possible importance of tetrahydro-α-naphthylamine in the technology of dyes, it appeared desirable to investigate more closely the formation of this base and also to attempt to prepare a number of its previously unknown deriv-

atives in order to compare their properties with those of benzenoid and naphthalenoid compounds of corresponding type.

ar-Tetrahydro-α-naphthylamine was obtained by Bamberger and Althausse (*Ber.*, 1888, **21**, 1786) by reducing α-naphthylamine with sodium and boiling amyl alcohol. This reaction appears to be a general one for the preparation of hydrogenated naphthalene derivatives, a considerable number of which were prepared by Bamberger and his numerous collaborators (*loc. cit.*). It is usually carried out by reducing a boiling solution of the substance in ten times its weight of amyl alcohol with one and a-half to twice the theoretical quantity of sodium (Bamberger and Lodter, *Ber.*, 1877, **20**, 3073). The yield and character of the product vary with the individual substance reduced, α-derivatives of naphthalene giving rise to aromatic, whereas β-derivatives form mainly alicyclic compounds. Thus it was found (Bamberger and Müller, *Ber.*, 1888, **21**, 850; Bamberger and Kitschelt, *Ber.*, 1890, **23**, 876) that the main product obtained by reducing β-naphthylamine was *ac*-tetrahydro-β-naphthylamine, together with a small quantity of *ar*-tetrahydro-β-naphthylamine. On the other hand, *ar*-tetrahydro-α-naphthylamine is stated to be the sole product when α-naphthylamine is reduced, the isomeric alicyclic compound having only been obtained from *ac*-tetrahydro-5-amino-1-naphthylhydrazine (Bamberger and Bammann, *Ber.*, 1889, **22**, 964).

The influence of the particular alcohol used as solvent on the yield of product was also investigated by Bamberger, who found that in the reduction of β-naphthylamine, replacement of amyl alcohol by ethyl alcohol results in a minimum yield of the tetrahydro-derivative, and concluded that the course taken by the reaction and the yield obtained were intimately connected with the boiling point of the solvent employed. Later experiments (Bamberger and Müller, *Ber.*, 1888, **21**, 1112), using such solvents as hexadecyl alcohol, phenol, glycerol, and mixtures of amyl alcohol and vaselin, did not, however, support this hypothesis, at least in the case of β-naphthylamine.

We have now studied the conditions governing the conversion of α-naphthylamine into *ar*-tetrahydro-α-naphthylamine. When amyl alcohol was used as the solvent and the reduction carried out as described by other workers, a yield of 70 per cent. of the theoretical was obtained. It was found that when amyl alcohol was replaced by ethyl alcohol, the α-naphthylamine remained unaltered and no *ar*-tetrahydro-α-naphthylamine could be detected. Similarly, α-naphthylamine was not changed by treatment with sodium when butyl alcohol was used as solvent, and the addition of butyl alcohol to amyl alcohol produced a diminution in yield

proportional to the quantity of butyl alcohol in the mixture. Moreover, in an experiment in which butyl alcohol was employed under pressure sufficient to raise the boiling point to that of amyl alcohol under normal pressure, no trace of *ar*-tetrahydro-α-naphthylamine could be detected. The difference in the behaviour of amyl alcohol from other alcohols cannot therefore be due to differences in boiling point, and as the reaction is always accompanied by the destruction of from 10 to 15 per cent. of the amyl alcohol used, it is probable that the reduction is intimately connected with the oxidation of amyl alcohol, and not simply due to direct hydrogenation.

The effect of the presence of (1) sodium amalgam, (2) mercurous chloride, (3) a nickel catalyst, (4) dextrose, on the reaction with sodium in butyl-alcoholic solution was also studied, but in no case could the tetrahydro-base be detected.

Sabatier and Senderens succeeded in preparing tetrahydronaphthalene by reducing naphthalene with hydrogen in the presence of nickel (*Compt. rend.*, 1901, **132**, 1254). We have now tried to prepare *ar*-tetrahydro-α-naphthylamine by the nitration and reduction of tetrahydronaphthalene. Although nitrations were carried out under a variety of conditions, in all cases oxidation took place and no nitro-derivative was isolated.

The *ar*-tetrahydro-α-naphthylamine required for our subsequent experiments was prepared by reducing a boiling amyl-alcoholic solution of α-naphthylamine with sodium The mixture was poured into water, the amyl alcohol layer separated, acidified with hydrochloric acid, and the amyl alcohol removed by distillation in a current of steam. The residue was filtered from a little tar and allowed to crystallise, when the hydrochloride of *ar*-tetrahydro-α-naphthylamine separated in large, colourless tables similar in appearance to aniline hydrochloride. The mother liquors from a number of preparations were united and concentrated, whereby a further quantity of the hydrochloride was obtained. The filtrate from this was basified, and the separated base examined. It was found that whereas pure *ar*-tetrahydro-α-naphthylamine condenses with 4-chloro-1:3-dinitrobenzene to form 2:4-dinitrophenyltetrahydro-α-naphthylamine, a compound crystallising in orange-red plates or needles melting at 134°, the base from the mother liquors when similarly treated gave, together with this compound, an isomeric substance crystallising in golden-yellow leaflets melting at 121°. The two compounds could be readily separated in a pure condition, as the former is less readily soluble in alcohol than the latter. This observation pointed to the presence in the mother liquors of *ac*-tetrahydro-α-naphthylamine. This was isolated by

passing carbon dioxide through a solution of the mixed bases in light petroleum, when the crude carbonate of the alicyclic compound separated. The base after purification proved to be identical with *ac*-tetrahydro-α-naphthylamine described by Bamberger and Bammann (*loc. cit.*).

α-Naphthylamine on reduction, therefore, gives mainly the *ar*-tetrahydro-base, together with a small quantity of the *ac*-tetrahydro-base, whereas in the case of β-naphthylamine the proportion of alicyclic and aromatic tetrahydro-bases is reversed.

B. *Nitro-derivatives of* ar-*Tetrahydro-α-naphthylamine.*

Morgan, Micklethwait, and Winfield (T., 1904, **85**, 737) state that the changes involved on nitrating *ar*-tetrahydro-α-naphthylamine and its acyl derivatives are somewhat complex. We have now examined the process more closely, and have prepared and examined the mono- and di-nitro-derivatives of *ar*-tetrahydroaceto-α-naphthalide and the corresponding nitroamines.

When *ar*-tetrahydroaceto-α-naphthalide is nitrated in cold sulphuric acid solution with one molecular proportion of nitric acid, a nitro-derivative is formed, together with a considerable proportion of an uncrystallisable resin. The formation of resins in this and other cases may possibly be due to the presence of a small quantity of the alicyclic isomeride in the material employed. The product proved to be a mononitro-compound. It is readily reduced to the monoacetyldiamine melting at 156°, which on treatment with acetic anhydride is converted into the diacetyldiamine, melting at 291°, described by Morgan, Micklethwait, and Winfield (*loc. cit.*). The nitro-group is therefore in the para-position with respect to the acylamino-group. In no case was the presence of the isomeric ortho-nitro-derivative detected.

The para-nitroamine itself is readily obtained by the hydrolysis of the acetyl derivative with alkalis or acids, and is similar in appearance and properties to *p*-nitroaniline. It is converted on reduction into *ar*-tetrahydro-1:4-naphthylenediamine.

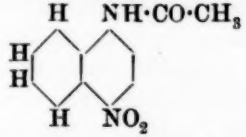
4-Nitro-*ar*-tetrahydro-α-naphthylamine may be diazotised and coupled, forming azo-dyes, the shades of which approximate more nearly to those of azo-dyes of similar type derived from benzenoid than from naphthalenoid bases.

When the quantity of nitric acid was increased to two molecular proportions and the nitration carried out as before, another product was obtained which, after separation from resinous impurities by crystallisation from alcohol, proved to be a dinitro-compound. This substance is also formed by the further nitration of 4-nitro-

ar-tetrahydroaceto-α-naphthalide. The dinitrotetrahydro-α-naphthylamine itself is readily obtained by warming the acetyl derivative with sulphuric acid.

Both the mono- and di-nitroamines form quinonoid salts with alkalis (compare T., 1913, **103**, 508). The mononitro-compound gives an orange-red potassium salt and the dinitro-compound a bluish-green potassium salt. In the former case, the salt dissociates rather more readily than we found to be the case with other quinonoid salts of nitroamines.

4-Nitro-ar-*tetrahydroaceto-α-naphthalide*,

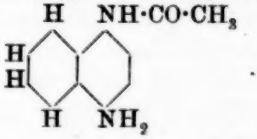


Ten grams of tetrahydroaceto-α-naphthalide, melting at 154°, prepared as described by Morgan, Micklethwait, and Winfield (*loc. cit*), were dissolved in 16 c.c. of 100 per cent. sulphuric acid. The solution was cooled to −10° in a freezing mixture and nitrated at that temperature by the addition of a mixture of 3·6 c.c. of nitric acid (one molecular proportion, D 1·4) and 9 c.c. of 100 per cent. sulphuric acid. On recrystallisation of the product from dilute alcohol or boiling water, *4-nitro*-ar-*tetrahydroaceto-α-naphthalide* was obtained in colourless, slender needles melting at 178°. It is readily soluble in organic solvents, but less readily so in water:

0·1864 gave 19·3 c.c. N_2 at 19° and 756 mm. N = 11·88.
$C_{12}H_{14}O_3N_2$ requires N = 11·96 per cent.

0·01248 required 10·1 c.c. $TiCl_3$ (1 c.c. = 0·001772 gram Fe). Calculated as $C_{10}H_{10}(NH{\cdot}CO{\cdot}CH_3){\cdot}NO_2$ = 99·85 per cent., that is, 6H required for reduction.

1-*Acetyl*-ar-*tetrahydro*-1 : 4-*naphthylenediamine*,



Five grams of iron powder, 1 gram of acetic acid (30 per cent.), and 15 c.c. of water were placed in a flask, and 6·5 grams of finely powdered 4-nitro-*ar*-tetrahydroaceto-α-naphthalide were added in small portions at a time. The flask was well shaken, and the

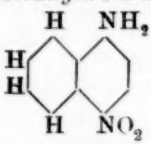
temperature rose as the reduction proceeded. When the contents of the flask had lost their yellow colour, the mixture was filtered hot and the residue boiled several times with water and filtered. The united filtrates were extracted with ether, and colourless, rhombic plates or needles of 1-*acetyl*-ar-*tetrahydro*-1 : 4-*naphthylenediamine*, melting at 156°, separated from the ethereal solution:

0·1452 gave 17·2 c.c. N_2 at 20° and 762 mm. N = 13·62.
$C_{12}H_{16}ON_2$ requires N = 13·72 per cent.

1·20 required 5·85 c.c. *N*-$NaNO_2$. Calculated as $C_{10}H_{10}(NH{\cdot}CO{\cdot}CH_3){\cdot}NH_2$ = 99·6 per cent.

It is readily soluble in water, dilute acids, or organic solvents. By treatment with acetic anhydride, it is converted into the diacetyldiamine, which forms colourless needles melting at 291°. It may be diazotised and combined with amines and phenols. For example, with 2-naphthol-3 : 6-disulphonic acid, a dye is formed which gives a reddish-brown shade on wool similar to that obtained with the corresponding compound derived from acetyl-*p*-phenylenediamine (Azo Corallin L).

4-*Nitro*-ar-*tetrahydro*-α-*naphthylamine*,



4-Nitrotetrahydroaceto-α-naphthalide is hydrolysed readily on boiling the alcoholic solution for ten minutes with sodium hydroxide. The nitroamine crystallises from the yellow solution on cooling, and on recrystallisation from dilute alcohol was obtained in pale yellow needles, melting at 116°. It is readily soluble in organic solvents or dilute acids, but less readily so in water. Hydrolysis may be effected equally well by boiling with dilute sulphuric acid or hydrochloric acid:

0·1236 gave 15·5 c.c. N_2 at 18° and 756 mm. N = 14·45.
$C_{10}H_{12}O_2N_2$ requires N = 14·58 per cent.

2·25 required 11·7 c.c. *N*-$NaNO_2$. Calculated as $C_{10}H_{12}(NO_2){\cdot}NH_2$ = 99·84 per cent.

0·01 required 9·9 c.c. $TiCl_3$ (1 c.c. = 0·001772 gram Fe). Calculated as $C_{10}H_{10}(NH_2){\cdot}NO_2$ = 100·18 per cent., that is, 6H required for reduction.

On adding hydrochloric acid to an alcoholic solution of 4-nitro-*ar*-tetrahydro-α-naphthylamine, the *hydrochloride* separates in colourless, crystalline needles, which are decomposed by water.

Potassium Salt of 4-*Nitro*-ar-*tetrahydro*-α-*naphthylamine*, $NH{:}C_{10}H_{10}{:}NO_2K$.

Nine c.c. of a solution containing 1 gram of potassium hydroxide in 30 c.c. of absolute alcohol were added to a solution of 1 gram of the nitroamine in 100 c.c. of dry benzene. The colour became orange-yellow, but no precipitate separated. When the alcohol was evaporated, however, an orange-red precipitate of the salt was produced, which was washed with dry benzene and ether. The salt is immediately hydrolysed by water, giving the parent nitroamine and potassium hydroxide in solution.

Titration with sulphuric acid gave K = 16·76 (mean).

$C_{10}H_{11}O_2N_2K$ requires K = 16·95 per cent.

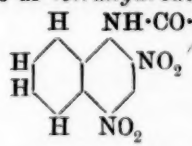
Cotton material padded with alkaline β-naphthol, dried, and passed through a bath of diazotised 4-nitro-*ar*-tetrahydro-α-naphthylamine, is coloured a bright orange-red as compared with the scarlet-red colour of "Para-red."

Diazotised 4-nitro-*ar*-tetrahydro-α-naphthylamine combines with salicylic acid, forming a yellowish-brown precipitate. This *dye* gives an orange-brown shade on chrome-mordanted wool as compared with the reddish-yellow shade which is obtained when chromed wool is dyed with *p*-nitrobenzeneazosalicylic acid (Alizarine Orange R).

4-Nitro-*ar*-tetrahydro-α-naphthylamine is readily reduced to the corresponding diamine by boiling stannous chloride. The colourless, crystalline product which separated was filtered off, dissolved in water, rendered alkaline with sodium hydroxide, and extracted with ether. Excess of acetic anhydride was added to the ethereal solution, and the precipitated diacetyl derivative crystallised from acetic acid. It formed colourless needles melting at 291°.

By oxidising a solution of the hydrochloride of the diamine with chromic acid, followed by extraction with ether, tetrahydro-α-naphthaquinone was obtained. After several crystallisations from light petroleum, it formed pale yellow needles melting at 55°, the temperature given by Bamberger and Lengfeld (*Ber.*, 1890, **23**, 1132).

2 : 4-*Dinitro*-ar-*tetrahydroaceto*-α-*naphthalide*,



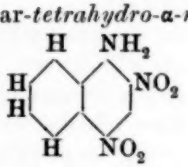
Ten grams of *ar*-tetrahydroaceto-α-naphthalide were dissolved in 16 c.c. of 100 per cent. sulphuric acid. The solution was cooled

to $-10°$ in a freezing mixture, and nitrated at that temperature by the addition of a mixture of 7·2 c.c. of nitric acid (two molecular proportions, D 1·4) and 24 c.c. of 100 per cent. sulphuric acid. The mixture was allowed to remain overnight at the ordinary temperature, and then poured on ice. The crude product was separated and crystallised twice from alcohol, when it formed colourless needles melting at 202°. The same substance is obtained by the further nitration of 4-nitro-*ar*-tetrahydroaceto-α-naphthalide:

0·1148 gave 16·3 c.c. N_2 at 18° and 754 mm. N = 16·36.
$C_{12}H_{13}O_5N_3$ requires N = 16·47 per cent.

0·00943 required 12·8 c.c. $TiCl_3$ (1 c.c. = 0·001772 gram Fe). Calculated as $C_{10}H_9(NH{\cdot}CO{\cdot}CH_3)(NO_2)_2 = 99·8$ per cent., that is, 12H required for reduction.

2:4-*Dinitro*-ar-*tetrahydro*-α-*naphthylamine*,



Dinitro-*ar*-tetrahydroaceto-α-naphthalide was conveniently hydrolysed by triturating to a paste with a little water and dissolving in concentrated sulphuric acid. The solution was warmed to 50° and poured into water. The yellow flocks which separated were collected and crystallised from alcohol. 2:4-*Dinitro*-ar-*tetrahydro*-α-*naphthylamine* forms small, yellow needles melting at 181°. It dissolves in dilute alkali hydroxide with a crimson colour:

0·1098 gave 16·7 c.c. N_2 at 19° and 765 mm. N = 17·65.
$C_{10}H_{11}O_4N_3$ requires N = 17·72 per cent.

0·01 required 19·5 c.c. $TiCl_3$ (1 c.c. = 0·001446 gram Fe). Calculated as $C_{10}H_9(NH_2)(NO_2)_2 = 99·85$ per cent., that is, 12H required for reduction.

Potassium Salt of Dinitro-ar-*tetrahydro*-α-*naphthylamine*.

Fifteen c.c. of alcoholic potassium hydroxide, obtained by dissolving 1 gram of potassium hydroxide in 30 c.c. of absloute alcohol, were added to 2 grams of dinitro-*ar*-tetrahydro-α-naphthylamine dissolved in 200 c.c. of dry benzene. A dark bluish-green precipitate of the salt separated, which was collected and washed with dry benzene and ether. The dry salt forms a bluish-

green powder which deflagrates on heating. It is soluble in excess of alcoholic potassium hydroxide with a crimson colour.

Titration with sulphuric acid gave K = 13·97 (mean).

$C_{10}H_{10}O_3N_3K$ requires K = 14·18 per cent.

C. *Nitro-derivatives of* ar-*Tetrahydro-α-naphthol.*

ar-Tetrahydro-α-naphthol, originally prepared by Bamberger and Althausse (*Ber.*, 1888, **21**, 1892) by diazotising *ar*-tetrahydro-α-naphthylamine and boiling the diazonium compound with sulphuric acid, was shown by Bamberger and Lengfeld (*Ber.*, 1890, **23**, 1127) to possess the properties of a phenol rather than of a naphthol. In preliminary experiments on the nitration of *ar*-tetrahydro-α-naphthol, we have found that direct nitration does not yield satisfactory results, the products being charred and tarry owing to oxidation. It appeared desirable, therefore, first to prepare a sulphonic acid of *ar*-tetrahydro-α-naphthol, and to use this compound for the nitration experiments.

When *ar*-tetrahydro-α-naphthol was treated with sulphuric acid at 100—110°, as in the sulphonation of phenol, it was largely destroyed and no sulphonic acid could be isolated. The same result was obtained when the temperature of sulphonation was reduced to 60—70°. Indirect methods of obtaining the sulphonic acid also failed. Thus, although sodium naphthionate is readily converted into 1-naphthol-4-sulphonic acid by treatment with sodium hydrogen sulphite, followed by boiling with alkali, its tetrahydro-derivative (sodium *ar*-tetrahydro-α-naphthylamine-4-sulphonate) does not react with sodium hydrogen sulphite, a fact dependent on its benzenoid character.

Further, diazotetrahydronaphthalene-4-sulphonic acid when boiled with dilute sulphuric acid gave, as sole product, *ar*-tetrahydro-α-naphthol, the sulphonic group being eliminated by hydrolysis during the reaction.

The *ar*-tetrahydro-α-naphtholmonosulphonic acid was eventually obtained by dissolving *ar*-tetrahydro-α-naphthol in twice its weight of cold concentrated sulphuric acid and allowing the solution to remain for two days. The product was very readily soluble in water, but its sodium salt could be isolated from the sulphonation mixture in the usual manner. On boiling the sulphonic acid with dilute acids, *ar*-tetrahydro-α-naphthol is regenerated.

From analogy to the monosulphonic acid of *ar*-tetrahydro-α-naphthylamine, which was shown by Morgan, Micklethwait, and Winfield (T., 1904, **85**, 742) to contain the sulphonic group in the para-position with respect to the amino-group, it was to be ex-

pected that the monosulphonic acid of *ar*-tetrahydro-α-naphthol would also be the para-compound. That this is the case is obvious from its behaviour on nitration and the properties of the nitro-derivatives.

The above authors, from a study of the reaction of diazonium compounds with 4-bromotetrahydro-α-naphthylamine and with *ar*-tetrahydro-α-naphthylamine-4-sulphonic acid, conclude that the reactivity of the hydrogen atom in the ortho-position with respect to the amino-group, which is such a characteristic feature of the naphthalene molecule, is destroyed when the non-substituted ring undergoes hydrogenation.

In the case of *ar*-tetrahydro-α-naphthol and its para-sulphonic acid, the behaviour towards diazonium compounds is rather different. *ar*-Tetrahydro-α-naphthol combines readily with diazonium compounds, forming azo-dyes. Yet this fact cannot be employed for estimating *ar*-tetrahydro-α-naphthol, as the figures obtained by titrating with *N*/10-*p*-nitrobenzenediazonium chloride solution are too high to agree with a simple para-azo-coupling and too low to agree with a complete formation of the bisazo-dye. This is in agreement with the observation made by Jacobson and Turnbull (*Ber.*, 1898, **31**, 898) that benzenediazonium chloride combines with *ar*-tetrahydro-α-naphthol, forming both the para-monoazo- and the bisazo-dye simultaneously. On the other hand, *ar*-tetrahydro-α-naphthol-4-sulphonic acid in alkaline solution does not combine with diazonium compounds to form azo-dyes. If, however, a diazonium compound is added to an acidified solution of *ar*-tetrahydro-α-naphthol-*p*-sulphonic acid and the mixture is rendered alkaline and then acidified, combination does takes place, the sulphonic group being displaced by the azo-group.

For the nitration experiments, it was found unnecessary to isolate the *ar*-tetrahydro-α-naphthol-4-sulphonic acid. The sulphonation mixture was diluted with water and nitrated with dilute nitric acid in the cold. Whereas all attempts at direct nitration of *ar*-tetrahydro-α-naphthol had proved unsatisfactory, approximately theoretical yields were obtained by nitrating the sulphonic acid under these conditions.

When one molecular proportion of nitric acid was used for nitration, the mixture set to a mass of yellow, needle-shaped crystals readily soluble in water, which proved to be a mononitro-*ar*-tetrahydro-α-naphtholsulphonic acid.

The sulphonic group of the nitrosulphonic acid was readily hydrolysed by boiling with dilute sulphuric acid. The product, mononitro-*ar*-tetrahydro-α-naphthol, is readily volatile with steam, forms orange-coloured salts with alkalis, and condenses with diazonium

compounds, forming azo-dyes. This behaviour is very similar to that of *o*-nitrophenol, and the compound is presumably an ortho-derivative.

By increasing the quantity of nitric acid to two and a-half molecular proportions and nitrating in the same manner, the nitrosulphonic acid separated as before, but on warming the mixture to 50°, the product became insoluble in cold water. This compound proved to be dinitro-*ar*-tetrahydro-α-naphthol.

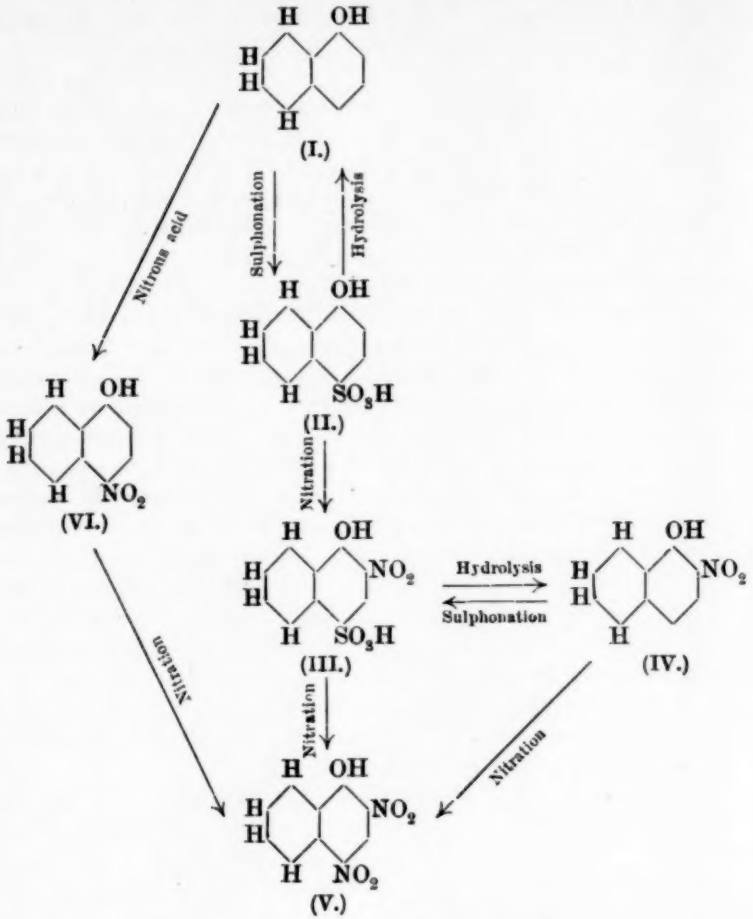
In order to obtain 4-nitro-*ar*-tetrahydro-α-naphthol, an attempt was made to prepare the corresponding nitroso-derivative. By the action of one molecular proportion of nitrous acid on *ar*-tetrahydro-α-naphthol, there was obtained, together with unaltered tetrahydro-α-naphthol, a product which crystallised in yellow needles melting at 163°. This substance did not give Liebermann's nitroso-reaction and was not affected by alkaline potassium ferricyanide. Analysis proved it to be a mononitro-*ar*-tetrahydro-α-naphthol. By increasing the amount of nitrous acid to two molecular proportions, the whole of the *ar*-tetrahydro-α-naphthol was converted into this nitro-compound. It was not volatile with steam, formed yellowish-brown salts with alkalis, and did not condense with diazonium compounds. The properties of the compound are similar to those of *p*-nitrophenol, and the substance is presumably the paranitro-derivative of tetrahydro-α-naphthol.

On further nitration, both mononitro-derivatives give rise to the above dinitro-compound. The relationship of these compounds is therefore shown by the scheme on p. 966.

On account of the importance of 2:4-dinitrophenol in the preparation of sulphide dyes by the action of the polysulphide fusion, it appeared of interest to examine the behaviour of dinitro-*ar*-tetrahydro-α-naphthol when subjected to a similar treatment. An equivalent quantity of this compound was substituted for 2:4-dinitrophenol in a technical process for the production of the well-known black sulphide dye (Sulphur Black T, etc.). The product possessed sulphide dyeing properties, but it was tinctorially weak and valueless.

ar-*Tetrahydro-α-naphthol* (I, p. 966).

The *ar*-tetrahydro-α-naphthol required in the following experiment was obtained by the method described by Bamberger and Althausse (*loc. cit.*). *ar*-Tetrahydro-α-naphthylamine was diazotised in the presence of excess of sulphuric acid, the mixture heated until the evolution of nitrogen ceased, and then distilled in a current of steam. The product formed shimmering, silvery plates



melting at 69° (Bamberger and Althausse give 68·5—69°). A further quantity of *ar*-tetrahydro-**α**-naphthol was prepared by Jacobson and Turnbull's modification (*Ber.*, 1898, **31**, 897) of Bamberger and Bordt's (*Ber.*, 1890, **23**, 215) method, consisting in the reduction of **α**-naphthol in boiling amyl-alcoholic solution with a large excess of sodium. Of the two methods of preparation, the former is to be preferred, owing to the fact that at least four times as much sodium is required to reduce **α**-naphthol completely to *ar*-tetrahydro-**α**-naphthol as is required to reduce **α**-naphthylamine to *ar*-tetrahydronaphthylamine.

ar-*Tetrahydro-α-naphthol*-4-*sulphonic Acid* (II, p. 966).

Ten grams of finely powdered *ar*-tetrahydro-α-naphthol were stirred into 20 grams of cold concentrated sulphuric acid. When completely dissolved, the solution was allowed to remain for two days at the ordinary temperature, and the mixture was then diluted with water and filtered from a trace of unsulphonated *ar*-tetrahydro-α-naphthol. The filtrate was neutralised with milk of lime, and the calcium salt, after removal of calcium sulphate, was converted into the sodium salt, evaporated to dryness, and the residue dissolved in a little water and alcohol added until the mixture was opalescent. On allowing to remain, *sodium* ar-*tetrahydro-α-naphthol*-4-*sulphonate* crystallised in colourless, prismatic needles. The crystals soon effloresce on exposure to air, leaving an amorphous powder. Both the sodium salt and the free sulphonic acid are very readily soluble in water. The sulphonic group is readily hydrolysed by boiling with dilute acids, *ar*-tetrahydro-α-naphthol being regenerated. ar-*Tetrahydro-α-naphthol*-4-*sulphonic acid* in neutral or alkaline solution does not couple with diazonium salts to form azo-compounds.

A sample of the sodium salt dried at 60° was employed in the following analysis:

0·2288 gave 0·2096 $BaSO_4$. S = 12·58.

$C_{10}H_{11}O_4SNa$ requires S = 12·80 per cent.

2-*Nitro*-ar-*tetrahydro-α-naphthol*-4-*sulphonic Acid* (III, p. 966).

Eight grams of *ar*-tetrahydro-α-naphthol were dissolved in 16 grams of cold concentrated sulphuric acid. The solution was allowed to remain for two days, diluted with 25 c.c. of water, cooled in ice, and nitrated with 3·7 c.c. of nitric acid (one molecular proportion, D 1·4) diluted with 8 c.c. of water. The nitrosulphonic acid separated in yellow needles, which were collected, and a further quantity was obtained by adding an excess of hydrochloric acid to the filtrate. The product was recrystallised by dissolving in a little water and adding hydrochloric acid. 2-*Nitro*-ar-*tetrahydro-α-naphthol*-4-*sulphonic acid* crystallises in long, pale yellow, flat needles melting at 182°, which are readily soluble in water or alcohol. It dissolves in dilute alkalis with a yellow colour, forming very readily soluble salts, and the free sulphonic acid is only reprecipitated by the addition of a large excess of acid. The sulphonic group is readily hydrolysed on boiling with dilute sulphuric acid (1 : 1).

An air-dried specimen was employed for the following analyses:

0·4158 gave 18·4 c.c. N_2 at 18° and 747 mm. N = 5·04.

0·2632 „ 0·2217 $BaSO_4$. S = 11·57.

$C_{10}H_{11}O_6NS$ requires N = 5·12; S = 11·72 per cent.

0·01 required 7·7 c.c. $TiCl_3$ (1 c.c. = 0·001556 gram Fe). Calculated as $C_{10}H_9(OH)(SO_3H)\cdot NO_2$ = 99·5 per cent., that is, 6H required for reduction.

2-Nitro-ar-*tetrahydro-α-naphthol* (IV, p. 966).

2-Nitro-*ar*-tetrahydro-α-naphthol-4-sulphonic acid was boiled with dilute sulphuric acid (1 : 1) and distilled in a current of steam. When crystallised from ether, *2-nitro*-ar-*tetrahydro-α-naphthol* forms long, yellow needles melting at 56°, which are readily soluble in organic solvents but sparingly so in water. It is readily volatile with steam and possesses a sweet, pleasant odour.

2-Nitro-*ar*-tetrahydro-α-naphthol dissolves in sodium hydroxide with an orange coloration. The *sodium* salt crystallises from a hot concentrated aqueous solution in orange-red, shimmering plates or needles.

2-Nitro-*ar*-tetrahydro-α-naphthol couples with diazonium compounds, forming azo-dyes. It may be estimated by titration with a standardised diazonium chloride solution:

0·2246 gave 14·1 c.c. N_2 at 18° and 747 mm. N = 7·14.

$C_{10}H_{11}O_3N$ requires N = 7·25 per cent.

0·01 required 11·6 c.c. $TiCl_3$ (1 c.c. = 0·001495 gram Fe). Calculated as $C_{10}H_{10}(OH)\cdot NO_2$ = 99·6 per cent., that is, 6H required for reduction.

0·3 required 15·4 c.c. *N*/10-*p*-nitrodiazobenzene. Calculated as $C_{10}H_{10}(OH)\cdot NO_2$ = 99·07 per cent.

4-Nitro-ar-*tetrahydro-α-naphthol* (VI, p. 966).

Ten grams of *ar*-tetrahydro-α-naphthol were dissolved in sodium hydroxide, the solution being diluted with water to 300 c.c. To this, an aqueous solution of 7·2 grams of sodium nitrite (two molecular proportions) was added, together with 200 grams of ice. One hundred c.c. of 10 per cent. sulphuric acid, contained in a dropping funnel, the end of which dipped below the surface of the liquid, were then slowly run into the mixture with constant agitation. The yellowish-white precipitate was collected and washed with cold water. The major portion dissolved in sodium carbonate solution, and was filtered from a small quantity of a tarry residue. From the filtrate, the product was precipitated by dilute acetic acid.

4-Nitro-ar-*tetrahydro-α-naphthol* crystallises from dilute alcohol

in yellow needles melting at 163°. It is not volatile with steam. It dissolves in sodium hydroxide with a yellowish-brown colour, and on the addition of excess of alkali the sodium salt crystallises in brown needles. Its salts are more readily soluble in water than those of the isomeric 2-nitro-compound.

4-Nitro-*ar*-tetrahydro-α-naphthol does not couple with diazonium compounds:

0·2432 gave 15·0 c.c. N_2 at 18° and 758 mm. N = 7·12.
$C_{10}H_{11}O_3N$ requires N = 7·25 per cent.

0·0103 required 11·4 c.c. $TiCl_3$ (1 c.c. = 0·001556 gram Fe). Calculated as $C_{10}H_{10}(OH)\cdot NO_2$ = 99·0 per cent., that is, 6H required for reduction.

2:4-*Dinitro*-ar-*tetrahydro-α-naphthol* (V, p. 966).

Twelve grams of *ar*-tetrahydro-α-naphthol were dissolved in 24 grams of cold concentrated sulphuric acid, the solution was allowed to remain for two days, and diluted with 32 c.c. of water. The clear liquid was cooled in ice and nitrated with 14 c.c. of nitric acid (2·5 molecular proportions, D 1·4) diluted with 16 c.c. of water. The 2-nitro-*ar*-tetrahydro-α-naphthol-4-sulphonic acid crystallised in a mass of yellow needles. The mixture was then warmed on the water-bath at 50° until the separated product was insoluble in cold water. The yield was almost theoretical. 2:4-*Dinitro*-ar-*tetrahydro-α-naphthol* crystallises from ether in large, yellow, rhombic prisms melting at 105°. The same substance is obtained by the further nitration of either 2- or 4-nitro-*ar*-tetrahydro-α-naphthol. It is also formed by nitrating diazotetrahydronaphthalene-4-sulphonic acid. It is soluble in organic solvents, sparingly so in hot water, and is slightly volatile with steam. It dissolves in sodium hydroxide with an orange-brown colour, and the *sodium* salt crystallises from the solution in orange needles:

0·2046 gave 20·4 c.c. N_2 at 18° and 764 mm. N = 11·63.
$C_{10}H_{10}O_5N_2$ requires N = 11·76 per cent.

0·01 required 18·8 c.c. $TiCl_3$ (1 c.c. = 0·001495 gram Fe). Calculated as $C_{10}H_9(OH)(NO_2)_2$ = 99·5 per cent., that is, 12H required for reduction.

D. α-*Chloro*-ar-*tetrahydronaphthalene.*

The preparation of 1-bromotetrahydronaphthalene from *ar*-tetrahydro-α-naphthylamine by the Sandmeyer reaction has been described by C. Smith (T., 1904, **85**, 729). Subsequently, Morgan,

Micklethwait, and Winfield prepared from it a bromodinitrotetrahydronaphthalene (T., 1904, **85**, 747).

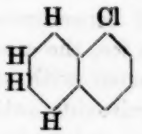
In view of the great reactivity of 4-chloro-1:3-dinitrobenzene, we have now prepared the corresponding chloro- and chlorodinitro-derivatives of tetrahydronaphthalene in order to study the behaviour of the latter compound.

When α-chloronaphthalene in boiling amyl-alcoholic solution is treated with sodium under the same conditions as are employed for the preparation of *ar*-tetrahydro-α-naphthylamine from α-naphthylamine, a mixture is obtained consisting of dihydronaphthalene, tetrahydronaphthalene, and unaltered α-chloronaphthalene. The dihydronaphthalene was identified by conversion into the dibromide, melting at 74° (Bamberger and Lodter, *Ber.*, 1887, **20**, 1706), and the tetrahydronaphthalene, by oxidation to *o*-carboxy-β-phenylpropionic acid, melting at 166° (Bamberger and Kitschelt, *Ber.*, 1890, **23**, 1564). No α-chlorotetrahydronaphthalene was formed by this method. It was therefore prepared directly from *ar*-tetrahydro-α-naphthylamine by Sandmeyer's reaction. The yield of α-chlorotetrahydronaphthalene obtained was not good, as a considerable proportion of *ar*-tetrahydro-α-naphthol and tetrahydronaphthalene was formed simultaneously. No improvement resulted from substituting copper powder for cuprous chloride in this reaction.

The product obtained by nitrating α-chlorotetrahydronaphthalene with two molecular proportions of nitric acid in the cold was largely contaminated with an uncrystallisable resin. Purification was effected by repeated extraction and crystallisation from light petroleum, in which solvent the resinous matter was sparingly soluble. When pure, the product, chlorodinitrotetrahydronaphthalene, crystallised in almost colourless plates or needles melting at 68°. It showed marked differences in behaviour towards amines, etc., from that exhibited by chlorodinitrobenzene. Thus, whilst the latter reacts readily with a hot alcoholic solution of hydrazine hydrate, the chlorodinitrotetrahydronaphthalene remains unaltered. It is also not attacked by aniline or other amines. This inactivity must probably be attributed to sterical hindrance.

On the other hand, both aromatic and alicyclic tetrahydro-α-naphthylamines condense with 4-chloro-1:3-dinitrobenzene, forming two isomeric dinitrophenyltetrahydro-α-naphthylamines. The condensation product in the former case crystallises in red leaflets melting at 134°, and in the latter in golden-yellow plates melting at 121°. Both these products were submitted to the action of the polysulphide fusion. No formation of dye occurred when the condenser method was employed, but sulphide dyes were formed in

each case when the temperature of the fusion was raised to 160—170°. The dye derived from dinitrophenyl-*ar*-tetrahydro-α-naphthylamine gave a bluish-green leuco-compound, whilst the leuco-derivative of the dye derived from dinitrophenyl-*ac*-tetrahydro-α-naphthylamine was olive-green. The dyes were tinctorially weak and dyed cotton grey from a sodium sulphide bath. Presumably condensation, resulting in the formation of a dye, occurs only at the dinitrophenyl end of the molecule in each case.

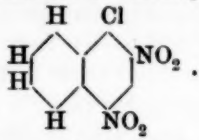
α-*Chloro*-ar-*tetrahydronaphthalene*,  .

Forty grams (1 mol.) of *ar*-tetrahydro-α-naphthylamine, 80 c.c. (2½ mols.) of hydrochloric acid, and 100 c.c. of water were ground into a fine paste and diazotised at 0° by the addition of a concentrated aqueous solution of the requisite amount of sodium nitrite. The clear yellow solution of the diazonium chloride was slowly run into a solution of cuprous chloride, prepared by heating 33 grams of cupric chloride with 15 grams of copper, 133 c.c. of hydrochloric acid, and 28 c.c. of water until colourless. The orange-red coloration produced with each addition of the diazonium salt rapidly disappeared on shaking. The mixture was then raised to the boiling point and distilled in a current of steam. The distillate, which consisted of a yellow, heavy oil, was washed with sodium hydroxide until free from *ar*-tetrahydro-α-naphthol. The insoluble oil was dried over calcium chloride and fractionated. The first fraction, distilling at 204—212°, contained tetrahydronaphthalene, and the second, distilling at 240—245°, contained α-chlorotetrahydronaphthalene. On refractionation, the major portion of the latter boiled at 250°/748 mm. *α-Chloro*-ar-*tetrahydronaphthalene* is a colourless, refractive liquid with an aromatic odour similar to that of chlorobenzene. Unlike α-chloronaphthalene, it does not form a crystalline picrate:

0·2528 gave 0·2164 AgCl. Cl = 21·17.

$C_{10}H_{11}Cl$ requires Cl = 21·32 per cent.

1-*Chloro*-2:4-*dinitro*-ar-*tetrahydronaphthalene*,



Six grams of α-chloro-*ar*-tetrahydronaphthalene were suspended in 20 c.c. of concentrated sulphuric acid and nitrated with a mixture of 5 c.c. of nitric acid (two molecular proportions, D 1·4) and 10 c.c. of concentrated sulphuric acid at 0°. The mixture was poured on ice, the crude product forming a brown, viscid mass. It was extracted with ether, and the ethereal solution washed with sodium hydroxide until all the yellowish-brown colour was removed. Rosettes of pale yellow needles surrounded by an uncrystallisable resin were deposited from the ethereal solution on keeping. After several crystallisations from light petroleum, the product was obtained in colourless plates or needles melting at 68°. It is readily soluble in organic solvents, is slightly volatile, and has a sweet odour:

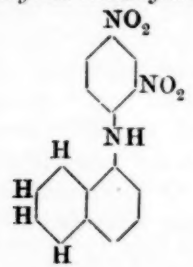
0·3426 gave 0·189 AgCl. Cl = 13·70.

0·2044 „ 19·3 c.c. N_2 at 20° and 754 mm. N = 10·75.

$C_{10}H_9O_4N_2Cl$ requires Cl = 13·84; N = 10·91 per cent.

0·01219 required 30·1 c.c. $TiCl_3$ (1 c.c. = 0·001062 gram Fe). Calculated as $C_{10}H_7(NO_2)_2Cl$ = 99·9 per cent., that is, 12H required for reduction.

2:4-*Dinitrophenyl*-ar-*tetrahydro*-α-*naphthylamine*,



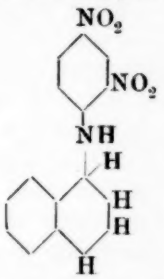
A mixture of 5 grams of *ar*-tetrahydro-α-naphthylamine and 6·9 grams of 4-chloro-1:3-dinitrobenzene was dissolved in 100 c.c. of alcohol, a hot solution of 4·6 grams of crystallised sodium acetate in a little water was then added, and the mixture boiled for eight hours under a reflux condenser. Condensation proceeds rather slowly. The dinitrophenyl-*ar*-tetrahydro-α-naphthylamine separates as it is formed in orange-red needles or plates. The product

crystallises from alcohol in red leaflets melting at 134°. It is readily soluble in acetone, benzene, or acetic acid, but less readily so in boiling alcohol and very sparingly so in cold alcohol. Addition of sodium hydroxide to the yellow alcoholic solution produces a deep red coloration:

0·1644 gave 18·9 c.c. N_2 at 18° and 758 mm. N = 13·28.
$C_{16}H_{15}O_4N_3$ requires N = 13·42 per cent.

0·01 required 8·4 c.c. $TiCl_3$ (1 c.c. = 0·002510 gram Fe). Calculated as $C_{16}H_{15}N(NO_2)_2$ = 99·87 per cent., that is, 12H required for reduction.

2:4-*Dinitrophenyl*-ac-*tetrahydro*-α-*naphthylamine*,



This compound, prepared in the same manner as the preceding, separates as an oil, which solidifies on cooling. It crystallises from alcohol in golden-yellow plates melting at 121°, which are more readily soluble than the isomeric compound. Addition of sodium hydroxide to the yellow alcoholic solution produces an orange-red coloration:

0·1482 gave 17·1 c.c. N_2 at 18° and 758 mm. N = 13·32.
$C_{16}H_{15}O_4N_3$ requires N = 13·42 per cent.

0·01 required 8·4 c.c. $TiCl_3$ (1 c.c. = 0·002510 gram Fe). Calculated as $C_{16}H_{15}N(NO_2)_2$ = 99·87 per cent., that is, 12H required for reduction.

In conclusion, we desire to express our thanks to Miss Eva Hibbert, who has kindly carried out the titanous chloride titrations of the nitro-compounds described, and to Messrs. Levinstein, Ltd., who have kindly supplied us with the materials required in this investigation.

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MANCHESTER.

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LXXXVIII.—*The* n-*Butylarylamines. Part I. The Action of* n-*Butyl Chloride on* o- *and* p-*Toluidines.*

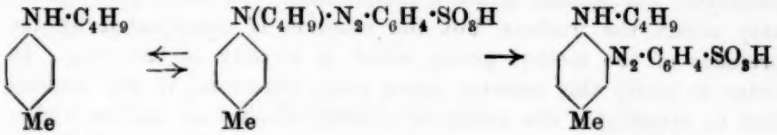
By Joseph Reilly and Wilfred John Hickinbottom.

Whilst the methyl- and ethyl-arylamines have been extensively investigated, the study of the members of this series containing larger alkyl groups has hitherto been practically neglected. Thus, in the case of the *n*-butylarylamines, with the exception of the *n*-butylanilines, so far as we are aware, no members of this group have been recorded in the literature. The aniline derivatives were prepared by the action of *n*-butyl chloride on the free base (T., 1917, **111**, 1026), and in the present investigation this reaction has been extended to the butylation of *o*- and *p*-toluidine. This was carried out by a similar method, and also by heating the amine with *n*-butyl alcohol in the presence of a condensing agent. From stereochemical considerations, the increase of the substituting alkyl group from a one- to a four-carbon chain may have a definite effect. In the chain of carbon atoms present in the *n*-butylarylamines, the terminal carbon atoms are probably nearer the nucleus than the corresponding carbon atoms in the lower alkyl derivatives. Consequently, the relation between these atoms and those in the benzene ring may be more intimate than if smaller carbon chains were present, and from the comparative study of these different types of compounds, light may be thrown on the question of ring formation.

When dealing with the alkylation of aniline, it was only necessary to take into account the entering group, but in the case of the toluidines, the influence of the group already in the ring has to be considered. *n*-Butyl chloride reacts with *p*-toluidine, producing both secondary and tertiary arylamines. In the reaction between *n*-butyl chloride and *o*-toluidine, however, it was found that mono-*n*-butyl-*o*-toluidine alone was obtained. Comparative experiments on the methylation and butylation of *o*-toluidine were carried out under conditions in which the dimethyl derivative was obtained. The corresponding di-*n*-butyl derivative, however, was not formed, the mono-*n*-butyl compound being the principal product. The introduction of the *n*-butyl group probably causes an accumulation of carbon atoms in Bischoff's "critical positions," which prevents any reaction between a second molecule of *n*-butyl chloride and the imino-group.

Regarding the two series of mono-*n*-butyltoluidines, on the one hand, with the para-compound, all migration to the para-position

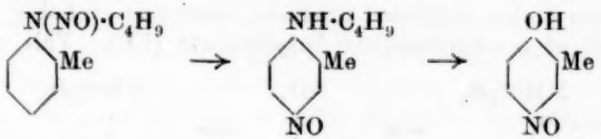
is prevented, as it is already occupied, whilst in the ortho-compound the formation of para-substituted derivatives is possible. Derivatives were therefore prepared of the two series in order to compare their properties. *o-Tolyl*-n-*butylnitrosoamine* in the presence of alcoholic hydrogen chloride yields the corresponding *p-nitroso*-compound, whilst when the nitrosoamine of *n*-butyl-*p*-toluidine is warmed with alcoholic hydrogen chloride, the nitroso-group is completely removed. Similarly, all attempts to effect a migration of the nitroso-group to the nucleus failed. On the other hand, it was found that by allowing diazotised sulphanilic acid to combine with *n*-butyl-*p*-toluidine (I) in acid solution, a mixture of diazoamino- and *o*-azo-compounds was obtained, namely, *4-methyl*-N-n-*butyldiazoaminobenzene-4′-sulphonic acid* (II) and 3-p-*sulphobenzeneazo*-n-*butyl*-p-*toluidine* (III). Under similar conditions,



(I.) (II.) (III.)

n-butylaniline gave almost exclusively the para-compound (this vol., p. 99).

The blue, crystalline *p*-nitroso-compound of *n*-butyl-*o*-toluidine (IV) has the property of forming additive compounds with metallic salts. The dark green, crystalline *cuprichloride* was isolated. By the action of alkali hydroxide on 5-nitroso-*n*-butyl-*o*-toluidine (V), this compound was decomposed, with the formation of *n*-butylamine and 5-nitroso-*o*-cresol, thus proving the migration of the nitroso-group in *o*-tolyl-*n*-butylnitrosoamine to the ring and establishing the orientation of the nitroso-compound.

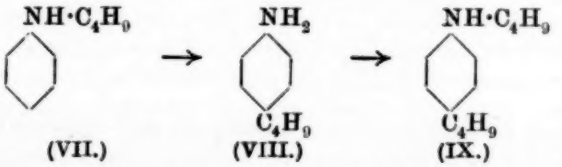


(IV.) (V.)

Di-*n*-butyl-*p*-toluidine is not affected to any appreciable extent by the action of nitrous acid for a short time, consequently the secondary and tertiary amines were separated by the use of this agent, the tertiary amine being recovered unchanged, whilst the secondary amine was obtained from the resulting nitrosoamine by the action of hydrochloric acid or by reduction. Another method available for the separation of the secondary and tertiary *n*-butyl-

p-toluidines depends on the difference in the physical properties of the picrates. The picrate of mono-*n*-butyltoluidine is an oil, whilst that of the di-*n*-butyl compound is a solid which is readily obtained in a crystalline form.

n-Butyl-*p*-toluidine was also obtained by heating *n*-butyl alcohol with *p*-toluidine hydrochloride. At about 140°, the secondary amine was produced, but on increasing the temperature, the yield diminished, and at about 240° no *n*-butyl-*p*-toluidine was isolated. Instead, a primary amine was collected in a fraction boiling between 255° and 270°. The other products consisted of a secondary amine of a higher boiling point, together with some ammonia, and a substance which had an odour resembling that of quinoline. The action of acids changed the latter substance to a resinous material. It is apparent that, even at the temperature employed, the reaction is not a simple one. The butyl group probably enters the nucleus, but the reaction is complicated by the presence of the methyl group which is already in the ring. In order to study this reaction more fully, therefore, it was decided first to investigate the action of *n*-butyl alcohol on aniline hydrochloride before proceeding to the more complex cases of *o*- and *p*-toluidine. The authors have already shown (this vol., p. 102) that *n*-butyl alcohol and aniline hydrochloride, when heated under pressure at a temperature below 200°, furnish mono-*n*-butylaniline (VII). The presence of a primary amine was also shown, and at the time this was assumed to be aniline. It is possible that a small quantity, at least, of a new amine was present. At higher temperatures, the amount of this amine increases. Thus, on heating a mixture of aniline hydrochloride and *n*-butyl alcohol in approximately molecular proportions to 240—280° for six to ten hours, the chief product was identified as p-*amino*-n-*butylbenzene* (VIII). It gives a *sulphate* which is almost insoluble in water. There were higher butylated products, consisting probably for the most part of p-n-*butylamino*-n-*butylbenzene* (IX). This reaction



(VII.) (VIII.) (IX.)

is interesting in that it throws some light on the production of alkyl nuclear substituted arylamines. The production of *p*-amino-*n*-butylbenzene would seem to follow from an intramolecular change of the *n*-butylaniline which is first produced. If this is the case, the reaction is remarkable in that it would indicate an

appreciable change in the stability of the alkyl-substituted anilines as the molecular weight of the alkyl group increases, especially when it is remembered that dimethylaniline may be produced in almost quantitative yield by the action of methyl alcohol on aniline at 220° in the presence of a catalyst. The production of *p*-toluidine from methylaniline is stated to require a temperature of 300°, yet it is possible to obtain *p*-amino-*n*-butylbenzene from aniline hydrochloride and *n*-butyl alcohol at as low a temperature as 200°. These results would indicate that the *n*-butyl group is attached to the nitrogen atom less firmly than is the methyl or ethyl group in corresponding compounds. *n*-Butyl alcohol readily loses water with the production of butylene, and it is possible that butylene, if formed, may react directly with the benzene nucleus with the production of a butylbenzene derivative. The question of the introduction of the *n*-butyl group into the benzene ring is being further investigated.

Experimental.

By heating *p*-toluidine with *n*-butyl chloride, both mono- and di-*n*-butyl-*p*-toluidines were formed. A solution of dry, powdered *p*-toluidine (1 mol.) in *n*-butyl chloride (2·5 mols.) was heated on a sand-bath under reflux until no more *n*-butyl chloride was condensed. This operation usually required sixty to eighty hours. By the addition of a small quantity of a substance such as iodine to the mixture, the time of heating was reduced. The contents of the flask, which were partly solid, contained the hydrochlorides of the mono- and di-alkyl-*p*-toluidines, together with some unchanged *p*-toluidine and *n*-butyl chloride. The unchanged *n*-butyl chloride was distilled off, the residue dissolved in water, treated with sodium carbonate or hydroxide solution, and the separated amines then removed by ether. To the ethereal extract an excess of zinc chloride solution (20 per cent.) was added, when *p*-toluidine zincichloride was precipitated. By washing the precipitate repeatedly with small amounts of ether, the mono- and di-substituted toluidines were removed, and were thus freed from the greater bulk of the *p*-toluidine. The ethereal layer was dried, and on removal of the ether an oil remained which, on distillation, gave crude mono-*n*-butyl-*p*-toluidine at 250—260°, and crude di-*n*-butyl-*p*-toluidine at above 260°.

Pure mono-*n*-butyl-*p*-toluidine was obtained by reducing its nitrosoamine with zinc dust and hydrochloric acid. The crude product (20 grams) was dissolved in a solution of 40 c.c. of concentrated hydrochloric acid in 100 c.c. of water, and then cooled

in ice. A slight excess of concentrated sodium nitrite solution was added to the cold mixture, when the nitrosoamine was formed, which was removed by extraction with ether. The ethereal extract was washed with alkali hydroxide and dried over potassium carbonate. The *p*-tolyl-*n*-butylnitrosoamine (20 grams), freed from ether, was mixed with concentrated hydrochloric acid (90 grams), and zinc dust gradually added in small amounts until an excess was present, the mixture being then heated on the water-bath for a short time. Excess of zinc dust was removed from the mixture by filtration, the zinc being washed several times with small amounts of absolute alcohol. The filtrate was acidified with hydrochloric acid and the alcohol removed by distillation. *n*-Butyl-*p*-toluidine was obtained from the acid residue by adding excess of sodium hydroxide solution, followed by ether extraction or steam distillation. The amine obtained in this manner usually contained a small quantity of substances which on distillation gave free ammonia. Traces of hydrazine might be produced during the reduction, and would be present in the amine. These impurities were removed by heating an ethereal solution of the crude *n*-butyl-*p*-toluidine with yellow mercuric oxide in the presence of alcohol under reflux. By using sodium hyposulphite for the reduction of the nitrosoamine in aqueous suspension or in aqueous-alcoholic solution, the greater part of the nitrosoamine was recovered unchanged.

The effect of heating the nitrosoamine with an excess of an *n*-butyl-alcoholic solution of hydrogen chloride was also investigated. On gently warming, a vigorous action ensued, oxides of nitrogen being evolved. Heating on the water-bath for six hours completed the reaction. Alcohol and water were distilled off, and, on keeping, the hydrochloride of the secondary amine crystallised out. This was purified either by boiling with animal charcoal followed by recrystallisation with water, or by converting it into the free base and passing dry hydrogen chloride into the benzene solution, when, on cooling, crystals of n-*butyl*-p-*toluidine hydrochloride* separated. These were collected and well washed with small amounts of cold benzene, when the hydrochloride was obtained as a white powder, which crystallised from alcohol in colourless, long, transparent needles or flattened prisms melting at 150—151°. By slow evaporation of the alcohol, crystals up to 5 cm. in length were obtained:

0·1988 gave 12·2 c.c. N_2 at 17° and 759 mm. N = 7·21.*
0·1116 „ 0·0804 AgCl. Cl = 17·82.
$C_{11}H_{17}N,HCl$ requires N = 7·02; Cl = 17·76 per cent.

* The nitrogen in every estimation was measured over 40 per cent. potassium hydroxide solution. Pressures corrected for vapour tension are recorded.

The hydrochloride is readily soluble in alcohol, water, or chloroform, less readily so in warm benzene or amyl acetate, sparingly so in cold benzene, and insoluble in ether or light petroleum.

n-*Butyl*-p-*toluidine*, obtained from the hydrochloride by the action of alkali hydroxide and extraction in the ordinary way, is an almost colourless oil boiling at 264—265°/766 mm. and miscible with most organic solvents. It distils in a current of steam:

0·1036 gave 0·3062 CO_2 and 0·0998 H_2O. C = 80·60; H = 10·70.
0·1043 ,, 7·95 c.c. N_2 at 20·5° and 751 mm. N = 8·76.
$C_{11}H_{17}N$ requires C = 80·91; H = 10·50; N = 8·58 per cent.

A hot alcoholic solution of *n*-butyl-*p*-toluidine, when treated with an excess of an alcoholic solution of oxalic acid, gave a precipitate of the sparingly soluble n-*butyl*-p-*toluidine oxalate*. It crystallises from hot alcohol in white, shining plates melting at 185°:

0·1870 gave 0·0410 CaO. $C_2H_2O_4$ = 35·20.
$C_{11}H_{17}N,C_2H_2O_4$ requires $C_2H_2O_4$ = 35·55 per cent.

The *picrate* was obtained as a viscous, red oil which did not readily solidify.

Aceto-n-*butyl*-p-*toluidide*.—The acetyl derivative was prepared by mixing the amine (7 grams) with three times its weight of acetic anhydride in the presence of a small quantity of zinc chloride. The mixture at first became very warm, and after the first reaction had subsided, the solution was heated on a sand-bath for half an hour to complete the acetylation. On pouring into water and extracting with ether, the *acetyl* compound separated from the ethereal solution as a very pale yellow, refractive oil which distilled at 294—295°/769 mm.:

0·2000 gave 12·35 c.c. N_2 at 19·3° and 754 mm. N = 7·16.
$C_{13}H_{19}ON$ requires N = 6·83 per cent.

Benzo-n-*butyl*-p-*toluidide*.—The *benzoyl* derivative, prepared by the Schotten-Baumann reaction, is a very viscous, pale yellow oil, distilling apparently unchanged at a temperature above 380° under the ordinary pressure:

0·3011 gave 12·90 c.c. N_2 at 18·8° and 746 mm. N = 4·92.
$C_{18}H_{21}ON$ requires N = 5·24 per cent.

p-*Tolyl*-n-*butylnitrosoamine*.—The crude nitrosoamine, prepared as above, was well washed first with dilute hydrochloric acid, then with sodium hydroxide solution, and finally with water. Distillation in a current of steam gave the nitrosoamine as a pale yellow oil having a slight red tinge:

0·1829 gave 23·7 c.c. N_2 at 18° and 735 mm. N = 14·70.

$C_{11}H_{16}ON_2$ requires N = 14·58 per cent.

The compound is practically insoluble in water, but soluble in most organic solvents. It is denser than water, readily volatile in a current of steam, and gives Liebermann's nitroso-reaction. By the action of an alcoholic solution of hydrogen chloride or by the action of sulphuric acid on its ethereal solution, no formation of nitrosoalkyltoluidine was observed.

By reducing the nitrosoamine in the cold with zinc dust and acetic acid, a mixture of bases was obtained containing some hydrazine derivative. Although *as*-*p*-tolyl-*n*-butylhydrazine has not been isolated, there is evidence that it is produced by the action of cold hydrochloric or acetic acid and zinc dust on *p*-tolyl-*n*-butylnitrosoamine. The amines are separated as hydrochlorides, and any *n*-butyl-*p*-toluidine hydrochloride produced is precipitated by cold benzene, in which it is only sparingly soluble; the dark solution, after removing the benzene, has reducing properties. By boiling under reflux an alcoholic or ethereal-alcoholic solution of the amine with mercuric oxide, metallic mercury is obtained. An aqueous solution of the hydrochloride reduces Fehling's solution slowly on boiling. If the amine is distilled under the ordinary pressure, ammonia is liberated, and the distillate darkens very rapidly in the air. These properties are in accordance with the assumption that a monoalkylhydrazine is present.

Di-n-*butyl*-p-*toluidine*.

From the fraction of the oil, boiling at above 260°, obtained by the action of *n*-butyl chloride on *p*-toluidine, by repeated fractional distillation, a pale yellow, refractive liquid, identified as the dialkylamine, was obtained which boiled at 282—284°/764 mm. It was also obtained pure from the crude mixture of mono- and di-*n*-butyl-*p*-toluidine by the following procedure. The mixed alkylamines were dissolved in excess of dilute hydrochloric acid and treated with nitrous acid. The nitrosoamine of the secondary base separated as an oil, and was removed by ether. The residue, after being heated for half an hour on the water-bath and then rendered alkaline, gave *di*-n-*butyl*-p-*toluidine*. It has only a faint odour. On exposure to light and air, the practically colourless oil slowly turns to a claret or dark red colour:

0·0596 gave 0·1799 CO_2 and 0·0618 H_2O. C = 82·33; H = 11·52.

0·1940 ,, 11·15 c.c. N_2 at 22·1° and 751 mm. N = 6·57.

$C_{15}H_{25}N$ requires C = 82·12; H = 11·49; N = 6·39 per cent.

Di-n-*butyl*-p-*toluidine* is soluble in the common organic solvents,

including acetic acid, and also in concentrated hydrochloric acid. When a solution of the base in an excess of dilute hydrochloric acid was treated with an aqueous solution of potassium ferrocyanide, a white precipitate of the *ferrocyanide* was obtained:

0·1000 gave 0·0174 Fe_3O_4. Fe = 12·6.

$C_{15}H_{25}N,H_4Fe(CN)_6$ requires Fe = 12·8 per cent.

It is a white powder, practically insoluble in water, ether, or alcohol. On exposure to air and light, the top layer very slowly turns green.

The *picrate* was obtained by shaking the crude amine with an excess of aqueous picric acid solution. It crystallises from a mixture of ether and light petroleum in pale yellow, rectangular crystals melting at 109—110°:

0·0706 gave 8·1 c.c. N_2 at 26° and 745·8 mm. N = 12·85.

$C_{15}H_{25}N,C_6H_3O_7N_3$ requires N = 12·50 per cent.

Titration with Titanous Chloride.—0·0104 required 17·3 c.c. $TiCl_3$ (1 c.c. = 0·001351 gram Fe). Calculated as

$C_{15}H_{25}N,C_6N_3O_7N_3$ = 100·2 per cent.

It is soluble in alcohol or acetone, moderately so in ether, and very sparingly so in light petroleum.

n-*Butyl-o-toluidine.*

By the action of *n*-butyl chloride on *o*-toluidine in the manner described in the case of *p*-toluidine, n-*butyl-o-toluidine* was prepared. By fractionating the oil obtained after removing most of the *o*-toluidine as the sparingly soluble zincichloride, *n*-butyl-*o*-toluidine was isolated as a colourless oil boiling at 258—260°/771 mm.

It is similar in general properties to the *n*-butyl-*p*-toluidine, has a faint, pleasant odour, and is lighter than water:

0·1360 gave 9·85 c.c. N_2 at 21° and 754·2 mm. N = 8·35.

$C_{11}H_{17}N$ requires N = 8·58 per cent.

As there was no fraction boiling above 260°, it would appear that di-*n*-butyl-*o*-toluidine is not formed under these conditions, and accordingly *n*-butyl-*o*-toluidine was heated on a sand-bath under reflux with a large excess of *n*-butyl chloride for ten days. Even after this period, it was not possible to isolate any di-*n*-butyl-*o*-toluidine, the product being for the most part unchanged mono-*n*-butyl-*o*-toluidine.

The monoalkyl compound gives an almost colourless *acetyl* derivative, which is an oil:

0·2044 gave 12·1 c.c. N_2 at 23° and 749·3 mm. N = 6·73.

$C_{13}H_{19}ON$ requires N = 6·83 per cent.

By the action of sodium nitrite solution on n-*butyl*-o-*toluidine* dissolved in hydrochloric acid, *o-tolyl*-n-*butylnitrosoamine* was obtained as a yellow oil, which is volatile in a current of steam and has a characteristic odour:

0·1038 gave 13·0 c.c. N_2 at 21° and 753·8 mm. N = 14·42.

$C_{11}H_{16}ON_2$ requires N = 14·58 per cent.

5-*Nitroso*-n-*butyl*-o-*toluidine Hydrochloride*.—By the action of alcoholic hydrogen chloride on the nitrosoamine in ethereal solution, the hydrochloride of the nitroso-derivative was obtained in good yield as a pale, greenish-yellow powder. On heating, it decomposed with a feeble explosion at 136°, darkening at a few degrees below that temperature:

0·1274 gave 0·0815 AgCl. Cl = 15·82.

$C_{11}H_{16}ON_2,HCl$ requires Cl = 15·51 per cent.

The *hydrochloride* is readily soluble in water, giving an intense yellow solution. It is also readily soluble in alcohol and practically insoluble in ether. The addition of a dilute solution of ammonia to an aqueous solution of the hydrochloride resulted in the precipitation of 5-*nitroso*-n-*butyl*-o-*toluidine*. Extraction with ether and removal of the solvent furnished the base as a green oil, which quickly solidified to a blue, crystalline compound. From a mixture of ether and light petroleum, it crystallised in masses of deep blue needles melting at 50°:

0·1448 gave 18·8 c.c. N_2 at 25° and 749·4 mm. N = 14·67.

$C_{11}H_{16}ON_2$ requires N = 14·58 per cent.

It is soluble in benzene, methyl alcohol, or acetone, moderately so in carbon disulphide, sparingly so in ether, and practically insoluble in light petroleum.

5-*Nitroso*-n-*butyl*-o-*toluidine Cuprichloride*.—The nitroso-base (2·5 mols.), dissolved in a small amount of hot methyl alcohol, was added to a hot aqueous methyl-alcoholic solution of cupric chloride (1 mol.). The mixture, on keeping overnight, deposited dark green crystals of the *cuprichloride*:

0·1573 gave 0·0837 AgCl. Cl = 13·2.

$(C_{11}H_{16}ON_2)_2,CuCl_2$ requires Cl = 13·5 per cent.

The nitroso-compound was decomposed by alkali hydroxide as follows. It was added to an excess of 10 per cent. sodium hydroxide solution, and steam passed into the solution. The colour rapidly became reddish-brown, and at the same time ammoniacal vapours were evolved, which were absorbed in hydrochloric acid

(20 per cent.). After the steam had passed in for about ten minutes, the residue in the flask was filtered, the filtrate slightly acidified with dilute sulphuric acid, and finally extracted with ether. From the ethereal solution, crystals were obtained which melted at 132—133°.

The compound had properties similar to those of 5-nitroso-*o*-cresol, and the hydrochloric acid solution was shown to contain *n*-butylamine. This decomposition confirmed the constitution of the nitroso-compound.

Action of n-*Butyl Alcohol on Primary Arylamine Salts.*

Pure *p*-toluidine hydrochloride (10 grams) was heated in a sealed tube with *n*-butyl alcohol (7·5 grams) at an initial temperature of 220°, gradually rising to 260°. The heating was stopped after seven to eight hours. On slowly cooling the tube, its contents partly solidified. In addition to the crystals, a dark brown, viscid liquid was present, and also a gas, which had an odour resembling that of butylene, burning with a smoky flame. On rendering the contents of the tube alkaline, an ammoniacal odour was perceived. On extraction with ether followed by distillation, the main fractions boiled between 220° and 300°, a residue being left in the flask. From the fraction boiling at 220—230°, a small amount of a substance was obtained of characteristic odour, which was insoluble in dilute hydrochloric acid solution and appeared to be resinified by concentrated hydrochloric acid.

The fraction boiling at 255—270° contained a considerable amount of a primary amine, with only a small quantity of a secondary amine. It was evident that the production of *n*-butyl-*p*-toluidine had not been realised, but that a more complicated reaction had occurred. The evidence points to the production of an aminobutyltoluene, and in order to study this type of reaction, the *p*-toluidine was substituted by aniline.

Aniline hydrochloride (1 mol.) was heated at 240—260° in a sealed tube with *n*-butyl alcohol (1·3 mols.) for seven to eight hours. On opening the cold tube, there was a slight pressure of gas, and the contents of the tube had partly crystallised. The product was rendered alkaline and distilled. A fraction boiling at 255—265° was obtained, which was characterised by yielding an insoluble *sulphate*, from which was prepared a primary amine boiling at 258—260°/750 mm. Its properties indicate that it is an *aminobutylbenzene*:

0·0745 gave 6·20 c.c. N_2 at 20·2° and 740·9 mm. N = 9·45.

$C_{10}H_{15}N$ requires N = 9·39 per cent.

It is a pale yellow oil which slowly becomes red. It is practically insoluble in water, and gives no characteristic colours with bleaching powder solution or with chromic acid. It can be diazotised, and the resulting diazonium salt combines with alkaline β-naphthol to yield a red *azo*-compound, which dissolves in concentrated sulphuric acid with a purple-red colour. This primary amine is being further studied.

*Combination of Mono-*n*-butyl-*p*-toluidine with Diazotised Sulphanilic Acid.*

Sulphanilic acid (2·5 grams) was diazotised, and the solution slowly added to a solution containing a similar weight of mono-*n*-butyl-*p*-toluidine in 30 grams of glacial acetic acid. The mixture rapidly became blood-red, but, after eight hours' shaking and then allowing the solution to remain for forty-eight hours, it was very dark in colour, whilst dark brown needles had separated. These were collected, and as they were very soft and viscid, they were kept for a few days in a vacuum desiccator over potassium hydroxide, when they were obtained as a hard, red mass of crystals. After being washed with water, in which they are only sparingly soluble, they were recrystallised from aqueous alcohol, and obtained in large, red, crystalline plates.

From the free acid, the *potassium* salt was prepared by adding a solution of potassium hydroxide (slightly more than 1 mol.) in methyl alcohol to a concentrated solution of the acid in absolute methyl alcohol. The potassium salt was precipitated as a bright red powder soluble in water, but sparingly so in absolute methyl alcohol:

0·1794 gave 0·0408 K_2SO_4. K = 10·2.

$C_{17}H_{20}O_3N_3SK$ requires K = 10·1 per cent.

The reduction of the crude potassium salt by means of sodium hyposulphite in warm aqueous solution gave, on making alkaline with sodium hydroxide, an oily layer, which became dark blue on keeping. The product contained a secondary amine, as shown by the action of nitrous acid, which gave *p*-tolyl-*n*-butylnitrosoamine. In addition, a diamine was present, probably an amino-*n*-butyl-*p*-toluidine, which was readily oxidised to a blue compound. The formation of the above two reduction products indicates that the product of combination contains the azo- and the diazoamino-compounds.

The pure *diazoamino*-compound was obtained by allowing the diazotised solution of sulphanilic acid to combine with the amine

in alcoholic solution under the following conditions. *n*-Butyl-*p*-toluidine (4·5 grams) was dissolved in alcohol (250 c.c.) and treated with a diazotised solution of sulphanilic acid (5 grams). The solution was shaken, and as the combination proceeded the colour changed to red. The addition of saturated sodium acetate solution, followed by removal of the alcohol on the water-bath, gave yellow crusts of the *sodium* salt of *4-methyl*-N-n-*butyldiazoaminobenzene-4'-sulphonic acid* in a crude form mixed with sodium acetate. The purified compound is sparingly soluble in concentrated sodium acetate solution, but soluble in water. The free diazoamino-compound was prepared by treating the aqueous solution of the sodium salt with a slight excess of dilute sulphuric acid (1 mol.) in the presence of an excess of ether, when the pale red, free acid was dissolved by the ethereal layer. Treatment of an absolute alcoholic solution of the acid with a slight excess of alcoholic potassium hydroxide gave a pale red precipitate of the *potassium* salt:

0·0775 gave 0·0180 K_2SO_4. K = 10·4.

$C_{17}H_{20}O_3N_3SK$ requires K = 10·1 per cent.

Reduction of the potassium salt in alkaline solution by means of hyposulphite gave a secondary amine which was isolated in the form of its hydrochloride. The amine was identified as *n*-butyl-*p*-toluidine.

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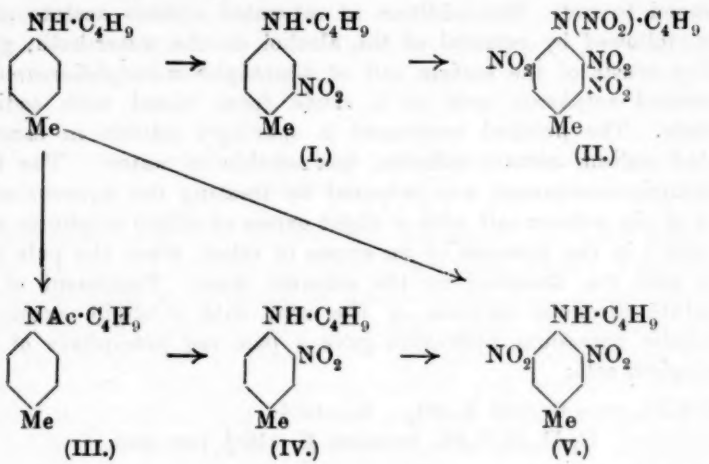
LXXXIX.—*The* n-*Butylarylamines. Part II. Nitration of Mono- and Di-*n-*butyl-*p-*toluidines.*

By Joseph Reilly and Wilfred John Hickinbottom.

The authors have made a study of the products of nitration of mono- and di-*n*-butyl-*p*-toluidine, which bases are described in the preceding paper. In the presence of an excess of sulphuric acid and the theoretical amount of nitric acid for the introduction of one nitro-group, the production of *2-nitro*-n-*butyl*-p-*toluidine* (I) proceeded smoothly, the pure compound being readily obtained from the recrystallised hydrochloride or sulphate. A more readily soluble portion, after precipitating the greater part of the 2-nitro-compound as the hydrochloride, contained small amounts of

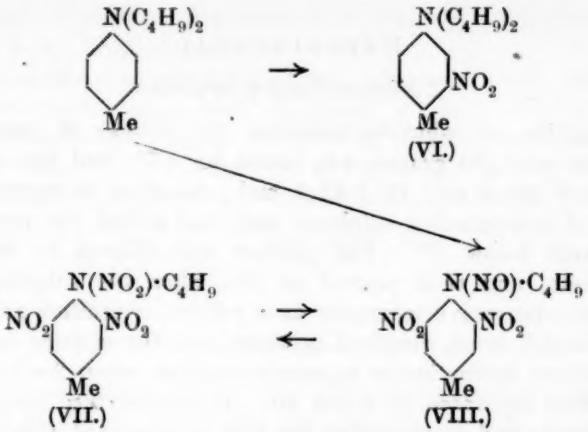
another nitro-compound. By using more than the calculated amount of nitric acid for the introduction of one nitro-group, a small amount of a white solid was isolated, crystallising in white needles melting at 122—125°.



When aceto-*n*-butyl-*p*-toluidide (III) was nitrated in acetic acid solution by means of fuming nitric acid, a nitroacetyl compound was obtained differing from that produced by the action of acetic anhydride on the 2-nitro-derivative. Hydrolysis by means of sulphuric acid (60 per cent.) yielded 3-*nitro*-n-*butyl*-p-*toluidine* (IV), which gave a soluble sulphate and hydrochloride.

By the action of nitric acid on a solution of the amine in glacial acetic acid, the chief product was 3:5-*dinitro*-n-*butyl*-p-*toluidine* (V), which is an orange-red, crystalline solid melting at 53—54°. Under more vigorous conditions, a pale yellow compound was formed, identical with that obtained by the action of nitrous acid on the dinitro-derivative, and was consequently the nitrosoamine, which, by further action of nitric acid, was converted into the corresponding nitroamine. When 2-nitro-*n*-butyl-*p*-toluidine was nitrated either by fuming nitric acid or by a mixture of sulphuric and nitric acids, a *trinitro*-p-*tolyl*-n-*butylnitroamine* (II) was produced, the nitro-groups being probably in the 2:3:5-positions.

The nitration of di-*n*-butyl-*p*-toluidine in sulphuric acid by means of the theoretical amount of nitric acid yielded 2-*nitrodi*-n-*butyl*-p-*toluidine* (VI), and nitric acid in glacial acetic acid gave the same nitrosoamine as was obtained from the monoalkyltoluidine under similar conditions, namely, 3:5-*dinitro*-p-*tolyl*-n-*butylnitrosoamine*.



It was considered that an examination of the products of nitration of *n*-butyl-*p*-toluidine would throw some light on the mechanism of nitration. With a small amount of nitric acid, a dinitro- and a mononitro-compound were obtained; on the other hand, with an excess of nitric acid, varying amounts of dinitro-*p*-tolyl-*n*-butylnitroamine and nitrosoamine were produced, the amount of the nitroamine increasing with the temperature. If the nitration proceeded with the intermediate product of nitroamines, some mononitro-*p*-tolyl-*n*-butylnitroamine should be obtained, as compounds of this type are relatively stable towards nitric acid (Pinnow, *Ber.*, 1897, **30**, 835).

When *p*-tolyl-*n*-butylnitrosoamine was nitrated by a solution of nitric acid in acetic acid, or by means of concentrated nitric acid, dinitro-*p*-tolyl-*n*-butylnitrosoamine was the usual product, the corresponding nitroamine only being produced by the further action of nitric acid. The reverse action, namely, the formation of the nitrosoamine from the nitroamine, can also be brought about. The production of the dinitroamine has not been observed, whilst the amount of dinitronitroamine formed was small and depended on the temperature at which the nitration was carried out, the amount increasing with the temperature. The results obtained by nitrating *n*-butyl-*p*-toluidine, and also *p*-tolyl-*n*-butylnitrosoamine, under different conditions would appear to be most readily explained by assuming that the nitration proceeds directly without the intermediate formation of a nitroamine.

Experimental.

2-*Nitro*-n-*butyl*-p-*toluidine*.

A solution of *n*-butyl-*p*-toluidine (10 grams) in concentrated sulphuric acid (40 grams) was cooled to −5°, and the calculated amount of nitric acid (D 1·42:1 mol.) dissolved in three times its weight of concentrated sulphuric acid was added, the temperature being kept below 10°. The product was allowed to remain for some time, and then poured on ice, when the sulphate of the mononitro-derivative separated as a yellow, crystalline solid. This was collected, dried, dissolved in water, and the solution neutralised with sodium hydroxide or ammonia solution, when 2-*nitro*-n-*butyl*-p-*toluidine* separated as a red oil. It was purified by preparing the sulphate and regenerating the base as described above:

0·1328 gave 15·10 c.c. N_2 at 16·6° and 756·0 mm. N = 13·33.

$C_{11}H_{16}O_2N_2$ requires N = 13·46 per cent.

This nitro-compound is soluble in most of the organic solvents. It is characterised by the ease with which it forms well-defined salts sparingly soluble in excess of the free acid used to precipitate them. The *sulphate* was obtained pure by recrystallising the crude sulphate from hot absolute alcohol and washing with a mixture of alcohol and ether. It forms white, shining plates darkening at 147—149° and melting at 152°:

0·1212 gave 9·6 c.c. N_2 at 18·1° and 752 mm. N = 9·19.

$C_{11}H_{16}O_2N_2,H_2SO_4$ requires N = 9·15 per cent.

The sulphate is easily hydrolysed by water; it is soluble in absolute alcohol or glacial acetic acid, but sparingly so in moderately concentrated sulphuric acid. The filtrate from the crude sulphate still contained an appreciable amount of the nitro-compound, which was obtained as the free base by rendering the solution alkaline and extracting with ether. The *hydrochloride* was prepared by treating the purified nitro-compound with an excess of concentrated hydrochloric acid. The precipitate was collected and dried in a vacuum desiccator over potassium hydroxide, when the salt was obtained as a white, crystalline compound which was readily hydrolysed by water. The hydrochloride was purified for analysis by crystallisation from absolute alcohol:

0·0738 gave 0·0438 AgCl. Cl = 14·68.

$C_{11}H_{16}O_2N_2,HCl$ requires Cl = 14·50 per cent.

The *hydrobromide* was prepared by adding aqueous hydrobromic acid to the base, when it was obtained as a crystalline precipitate. This salt is more readily soluble than the corresponding hydro-

chloride, and is readily hydrolysed by water. It crystallises from alcohol in white, shining plates.

2-*Nitroaceto*-n-*butyl*-p-*toluidide* was prepared by warming 2-nitro-*n*-butyl-*p*-toluidine with an excess of acetic anhydride in the presence of a very small quantity of concentrated sulphuric acid or of fused zinc chloride. It was obtained as a yellow oil, which solidified to a mass of pale yellow needles melting at 48—49°:

0·1032 gave 9·9 c.c. N_2 at 25° and 748·3 mm. N = 10·82.

$C_{13}H_{18}O_3N_2$ requires N = 11·20 per cent.

2-*Nitro*-p-*tolyl*-n-*butylnitrosoamine*.

Two grams of 2-nitro-*n*-butyl-*p*-toluidine sulphate were triturated with 10 c.c. of glacial acetic acid, the solution was then diluted by the addition of crushed ice, and a slight excess of the calculated amount of sodium nitrite solution gradually added. The mixture was poured into an excess of water, followed by extraction with ether. After washing the ethereal solution with sodium hydroxide solution and drying, the nitrosoamine was obtained as a pale yellow oil:

0·1028 gave 15·65 c.c. N_2 at 19·2° and 759 mm. N = 17·77.

$C_{11}H_{15}O_3N_3$ requires N = 17·72 per cent.

2-*Nitro*-p-*tolyl*-n-*butylnitrosoamine* is soluble in most organic solvents, sparingly so in light petroleum, and insoluble in water. It gives Liebermann's nitroso-reaction.

3-*Nitro*-n-*butyl*-p-*toluidine*.

This compound could not be conveniently prepared by direct nitration, consequently it was obtained by the hydrolysis of the corresponding 3-nitroaceto-*n*-butyl-*p*-toluidide. The latter compound was prepared by the following method. To a solution of aceto-*n*-butyl-*p*-toluidide (4 grams) dissolved in six times its weight of glacial acetic acid, nitric acid (D 1·5 : 30 grams) was added slowly, the temperature being kept below 20°. After the mixture had remained for some days, it was poured into a mixture of ice and water, and the free acid neutralised with sodium carbonate solution. A brownish-yellow oil was obtained, which solidified after remaining for a few hours in the ice-chest. After being crystallised several times from aqueous alcohol, it separated in pale yellow, square crystals melting at 68°:

0·0786 gave 7·45 c.c. N_2 at 19·1° and 750 mm. N = 10·93.

$C_{13}H_{18}O_3N_2$ requires N = 11·20 per cent.

Titration with Titanous Chloride.—0·0096 required 9·5 c.c. $TiCl_3$ (1 c.c. = 0·001351 gram Fe). Calculated as $C_{13}H_{18}O_3N_2$ = 99·8 per cent.

3-*Nitroaceto*-n-*butyl*-p-*toluidide* is very readily soluble in ethyl acetate or benzene, moderately so in ether or alcohol, but practically insoluble in light petroleum or water.

3-*Nitro*-n-*butyl*-p-*toluidine* was prepared by gently boiling the nitroacetyl compound with twenty-five times its weight of sulphuric acid (D 1·47). The colour became deeper, and finally, after about thirty minutes' heating, it was almost black. After remaining overnight, the nitro-derivative was obtained by neutralising with sodium carbonate solution and extraction with ether, when it was left as a red oil on removing the solvent:

0·1568 gave 18·25 c.c. N_2 at 20° and 749 mm. N = 13·37.

$C_{11}H_{16}O_2N_2$ requires N = 13·46 per cent.

Titration with Titanous Chloride.—0·02429 requires 20·0 c.c. $TiCl_3$ (1 c.c. = 0·00196 gram Fe). Calculated as $C_{11}H_{16}O_2N_2$ = 100·2 per cent.

The substance is distinguished from the corresponding 2-nitro-compound in giving a more readily soluble sulphate and hydrochloride.

3:5-*Dinitro*-n-*butyl*-p-*toluidine*.

Mono-*n*-butyl-*p*-toluidine (5 grams) was dissolved in ten times its weight of glacial acetic acid, and a solution of nitric acid (D 1·5: 30 grams) in glacial acetic acid (10 grams) added slowly. After a few hours, the mixture was poured on ice, when a red oil separated which, after extracting with ether and removal of the solvent, slowly acidified in the ice-chest to a mass of red needles. The compound crystallised from methyl alcohol in orange-red needles melting at 53—54°:

0·0713 gave 10·3 c.c. N_2 at 20° and 737 mm. N = 16·32.

$C_{11}H_{15}O_4N_3$ requires N = 16·60 per cent.

Titration with Titanous Chloride.—0·0118 requires 16·3 c.c. $TiCl_3$ (1 c.c. = 0·001914 gram Fe). Calculated as $C_{11}H_{15}O_4N_3$ = 100 per cent.

It is insoluble in water, moderately soluble in light petroleum or cold methyl alcohol, and readily so in acetone, ether, benzene, or carbon tetrachloride.

On warming 3:5-dinitro-*n*-butyl-*p*-toluidine (1 mol.) with acetic anhydride (2 mols.) and one drop of sulphuric acid, and then neutralising with sodium carbonate solution, 3:5-*dinitroaceto*-n-*butyl*-p-*toluidide* was obtained as a dark-coloured oil which slowly

solidified to a dark, crystalline mass. By extraction with aqueous alcohol and repeated crystallisation from a mixture of light petroleum and acetone, it was obtained in clusters of very pale yellow needles melting at 55—56°:

0·0704 gave 8·8 c.c. N_2 at 25° and 753·4 mm. N = 14·20.

$C_{13}H_{17}O_5N_3$ requires N = 14·24 per cent.

Titration with Titanous Chloride.—0·0109 requires 18·5 c.c. $TiCl_3$ (1 c.c. = 0·001351 gram Fe). Calculated as $C_{13}H_{17}O_5N_3$ = 100·8 per cent.

It is readily soluble in the usual solvents, sparingly so in light petroleum, and insoluble in water. The addition of a warm concentrated solution of potassium hydroxide to an alcoholic solution gives a purple coloration at the junction of the two liquids.

3:5-*Dinitro*-p-*tolyl*-n-*butylnitrosoamine* (VIII, p. 987).

3:5-Dinitro-*n*-butyl-*p*-toluidine (1 mol.) was dissolved in ten times its weight of glacial acetic acid, the solution cooled to 5°, and a solution of nitrous acid in acetic acid added. On allowing to remain for one hour and pouring on ice, the nitrosoamine separated as a yellow solid. It crystallised from aqueous methyl alcohol in pale yellow plates melting at 56—57°:

0·0708 gave 12·45 c.c. N_2 at 25·6° and 743·4 mm. N = 19·67.

$C_{11}H_{14}O_5N_4$ requires N = 19·86 per cent.

The nitrosoamine is insoluble in water, but readily soluble in most of the common organic solvents except light petroleum, in which it is only sparingly soluble. It responds to Liebermann's test for nitrosoamines. It is acted on by alkali hydroxides, a purple colour being produced, which changes to deep red. Light changes the colour from yellow to red. This nitrosoamine is also readily obtained by the nitration of *n*-butyl-*p*-toluidine under more vigorous conditions than those required for the production of the dinitro-compound. The nitration of *n*-butyl-*p*-toluidine as described above furnishes the nitrosoamine even if the mixture is allowed to remain for three weeks. During this time the colour changes, gradually becoming a darker red after a few hours, until it is almost black; after this the colour gradually becomes paler again, finally a pale yellow. The nitration was repeated, using less acetic acid, so that the mixture became warm. In this case, the change from the dark colour to the pale yellow took place rapidly, and, after twelve hours, the nitrosoamine was precipitated by pouring on ice. It was also prepared by nitrating *p*-tolyl-*n*-butylnitrosoamine in glacial acetic acid. A solution of the nitrosoamine

(3·3 grams) in glacial acetic acid (20 grams) was cooled in a freezing mixture, and a solution of nitric acid (D 1·5: 22 grams) in glacial acetic acid (10 grams) added slowly. The mixture was allowed to remain until the dark colour had changed to a pale yellow, when the product was found to be chiefly 3:5-*dinitro*-p-*tolyl*-n-*butylnitrosoamine*, and was very pale yellow. When this nitration was repeated, using a larger amount of nitric acid and allowing the mixture to become hot, the product had a considerably higher melting point than the nitrosoamine. Its manner of preparation and its reactions show that it is 3:5-dinitro-*p*-tolyl-*n*-butylnitroamine.

Under the following conditions, the compound can be produced in good yield. *p*-Tolyl-*n*-butylnitrosoamine (10 grams) was dissolved in glacial acetic acid (30 grams), and nitric acid (80 grams) added slowly with cooling, the temperature being kept below 30°. When the dark red colour of the solution had given place to a pale yellow, the mixture was warmed to 80—90° for an hour. On pouring into water, 3:5-dinitro-*p*-tolyl-*n*-butylnitroamine was precipitated as a white solid. After several crystallisations from aqueous alcohol (80 per cent.), it formed faintly yellow needles melting at 95°.

The action of fuming nitric acid on *p*-tolyl-*n*-butylnitrosoamine is extremely vigorous, but it was found possible to nitrate this compound by using a weaker acid at first and completing the reaction with the strong acid (D 1·5). To 11·4 grams of the nitrosoamine, 45 grams of nitric acid (D 1·4) were added gradually with cooling. After the mixture had remained for a short time, 60 c.c. of nitric acid (D 1·5) were added, and the mixture was then heated at 80—100° for about five minutes. On pouring into water, 3:5-dinitro-*p*-tolyl-*n*-butylnitroamine was obtained as a pale yellow solid. It was purified by extracting it three times with hot water and recrystallising from aqueous alcohol (80 per cent.). It was also obtained readily from 3:5-dinitro-*p*-tolyl-*n*-butylnitrosoamine by dissolving the latter in nitric acid (D 1·5) and allowing the solution to remain. The nitroamine crystallised in almost colourless needles. After filtering through glass wool and washing with water, it was obtained pure by one crystallisation from methyl alcohol:

0·0694 gave 0·1130 CO_2 and 0·0280 H_2O. C = 44·40; H = 4·48.
0·0706 „ 11·8 c.c. N_2 at 25·5° and 746·5 mm. N = 18·78.
$C_{11}H_{14}O_6N_4$ requires C = 44·28; H = 4·73; N = 18·79 per cent.

3:5-*Dinitro*-p-*tolyl*-n-*butylnitroamine* is readily soluble in most of the common organic solvents, sparingly so in light petroleum,

and almost insoluble in water. On gently warming with sulphuric acid and phenol, as in Liebermann's reaction, a green coloration is obtained which changes, on dilution, through a succession of colours to reddish-brown. This coloration reverts to green on rendering alkaline. An alcoholic solution of potassium hydroxide produces a red coloration, which becomes much darker on warming. A dilute solution of potassium cyanide when added to a solution of the nitroamine gives no coloration, but on warming the solution becomes brown.

2:3:5-*Trinitro*-p-*tolyl*-n-*butylnitroamine*.

To 2-nitro-*n*-butyl-*p*-toluidine (4 grams), 45 grams of nitric acid (D = 1·5) were added slowly so that the temperature of the mixture was 30—60°. The reaction was completed by heating at 80—90° for a short time. On pouring the mixture on ice, the compound separated in a crystalline form, and on recrystallisation from aqueous alcohol it was obtained in white needles melting at 87—88°:

0·0754 gave 13·4 c.c. N_2 at 22·5° and 757·3 mm. N = 20·46.

$C_{11}H_{13}O_8N_5$ requires N = 20·41 per cent.

It is readily soluble in benzene or chloroform, moderately so in cold methyl alcohol, but readily so in the boiling solvent. By using less nitric acid, a product was obtained melting at 80° after several crystallisations from aqueous alcohol. On crystallisation from nitric acid, the melting point was raised to 87—88°, and a mixture of this compound with 2:3:5-trinitro-*p*-tolyl-*n*-butylnitroamine also melted at 87—88°. The original compound before crystallisation from nitric acid was therefore the nitrosoamine.

2 : 3 : 5-*Trinitro*-p-*tolyl*-n-*butylnitrosoamine*.—Finely powdered 2-nitro-*n*-butyl-*p*-toluidine sulphate (2 grams) was gradually added to a mixture of nitric acid (D 1·4 : 14 grams) and concentrated sulphuric acid (33 grams), and the mixture kept at 30—35° for two hours. The reaction was completed by heating on the water-bath for five minutes. On pouring the mixture on ice, a viscid, sulphur-yellow product was obtained after washing with cold water, and after several crystallisations from aqueous alcohol it was obtained in very pale yellow crystals melting at 80·5°:

0·0734 gave 14·1 c.c. N_2 at 23° and 743·3 mm. N = 21·67.

$C_{11}H_{13}O_7N_5$ requires N = 21·41 per cent.

*Nitration of Di-*n*-butyl-*p*-toluidine.*

Di-*n*-butyl-*p*-toluidine was nitrated under conditions similar to those used in the nitration of mono-*n*-butyl-*p*-toluidine, namely, using an excess of nitric acid in glacial acetic acid, and by nitration in the presence of an excess of sulphuric acid.

Nitration by means of fuming nitric acid in glacial acetic acid proceeded vigorously, the reaction being controlled, when necessary, by the addition of a further quantity of acetic acid and by cooling. The product was isolated in the usual way, and, after recrystallisation from absolute methyl alcohol, melted at 57°. Analysis (Found: N = 19·85. Calc.: N = 19·86 per cent.) showed that the compound was 3:5-dinitro-*p*-tolyl-*n*-butylnitrosoamine, and a mixture of this compound obtained from 3:5-dinitro-*n*-butyl-*p*-toluidine by the action of nitrous acid with the above product also melted at 57°. By vigorous nitration, one of the alkyl groups of dibutyl-*p*-toluidine is therefore removed. It was observed that after the nitration mixture had been poured on ice and then allowed to remain for a short time, there was an odour resembling that of propionic acid or one of the lower members of the fatty acid series.

Di-*n*-butyl-*p*-toluidine (1 mol.) dissolved in a large excess of concentrated sulphuric acid was nitrated by the addition of the calculated amount of nitric acid (1 mol.) also dissolved in concentrated sulphuric acid. It gave 2-nitro-di-*n*-butyl-*p*-toluidine, which was isolated in the usual manner after pouring the mixture on ice and rendering alkaline:

0·0836 gave 8·16 c.c. N_2 at 28° and 742·3 mm. N = 10·81.

$C_{15}H_{24}O_2N_2$ requires N = 10·60 per cent.

*2-Nitrodi-*n*-butyl-*p*-toluidine*, which was obtained as a red oil, is miscible with most of the common organic solvents. It forms salts which are hydrolysed by water, and is characterised by its *hydrochloride*, which is obtained as a white precipitate on adding an excess of concentrated hydrochloric acid to an aqueous suspension of the base:

0·1247 gave 0·0610 AgCl. Cl = 12·11.

$C_{15}H_{24}O_2N_2,HCl$ requires Cl = 11·79 per cent.

Titration with Titanous Chloride.—0·0099 required 8·2 c.c. $TiCl_3$ (1 c.c. = 0·001351 gram Fe). Calculated for $C_{15}H_{24}O_2N_2,HCl$ = 100·4 per cent.

In order to determine the position of the nitro-group, the substance was further nitrated. To a solution of it (1 mol.) in ten times its weight of glacial acetic acid, forty times its weight of

nitric acid (D 1·5) was added slowly. After the mixture had remained for two or three hours, it was heated on the water-bath until the evolution of nitrous fumes ceased. On pouring into water, a pale yellow oil was obtained, solidifying to a brown mass, which on crystallisation from alcohol gave almost white needles melting at 80° (Found: N = 21·3), and a mixture of these with the product obtained by nitrating 2-nitro-*n*-butyl-*p*-toluidine melted at the same temperature. It was therefore 2:3:5-trinitro-*p*-tolyl-*n*-butylnitrosoamine (Calc.: N = 21·41 per cent.). If the nitro-group in the original compound were in position 3, then a dinitromono-butyl-*p*-tolyl derivative might be expected. On the other hand, 2-nitrodi-*n*-butyl-*p*-toluidine would be expected by vigorous nitration to lose a butyl group and yield the same product as 2-nitromono-*n*-butyl-*p*-toluidine. This was actually found to be the case. The evidence, therefore, is in favour of the view that the nitro-group in the mononitro-compound obtained by nitrating di-*n*-butyl-*p*-toluidine in sulphuric acid is in the ortho-position with respect to the methyl group.

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Stanni- and **stanno-chlorides**, organic (DRUCE), 715.

V.

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W.

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FORMULA INDEX.

THE following index of organic compounds of known empirical formula is arranged according to Richter's system (see *Lexikon der Kohlenstoff-Verbindungen*).

The elements are given in the order C, H, O, N, Cl, Br, I, F, S, P, and the remainder alphabetically.

The compounds are arranged—

Firstly, in groups according to the number of carbon atoms (thus C_1 group, C_2 group, etc.).

Secondly, according to the number of other elements besides carbon contained in the molecule (thus 5 IV indicates that the molecule contains five carbon atoms and four other elements).

Thirdly, according to the nature of the elements present in the molecule (given in the above order).

Fourthly, according to the number of atoms of each single element (except carbon) present in the molecule.

Salts are placed with the compounds from which they are derived. The chlorides, bromides, iodides, and cyanides of quaternary ammonium bases, however, are registered as group-substances.

C_1 Group.

CH_4 Methane, ignition of mixtures of air and (MASON and WHEELER), 45; (WHEELER), 840.

CCl_4 Carbon tetrachloride, action of aniline with (HARTUNG), 163.

1 II

CH_2O Formaldehyde, action of carbamide and (DIXON), 238.

CH_3I Methyl iodide, relative activities of ethyl iodide, propyl iodide and, with sodium α- and β-naphthoxides (Cox), 666.

$COCl_2$ Carbonyl chloride, action of ammonia with (WERNER), 694.

1 III

CHON Cyanic acid, metallic salts, hydrolysis of, 84.

CH_4ON_2 Carbamide, synthesis of (WERNER and CARPENTER), 694; mechanism of the synthesis of, from urethane (WERNER), 622; decomposition of, on heating with acids and with alkalis (WERNER), 84; interaction of formaldehyde and (DIXON), 238.

C_2 Group.

C_2H_5I Ethyl iodide, relative activities of methyl iodide, propyl iodide and, with sodium α- and β-naphthoxides (Cox), 666.

C_2H_6O Ethyl alcohol, association of organic compounds in solution in (INNES), 410.

C_2H_7N Ethylamine, preparation of (WERNER), 899.

2 III

$C_2H_4O_2N_2$ Oxamide, formation of urea and of biuret from (WERNER and CARPENTER), 694.

$C_2H_6ON_2$ Glycollamidine, salts of (RULE), 17.

$C_2H_6O_2N_2$ Methylolcarbamide, preparation of (DIXON), 246.

C_3 Group.

C_3H_7I *n*-Propyl iodide, relative activities of methyl iodide, ethyl iodide and with sodium α- and β-naphthoxides (Cox), 666.

3 III

$C_3H_7O_2N$ Urethane, mechanism of the synthesis of urea from (WERNER), 622.

C_4 Group.

C_4H_9Cl *n*-Butyl chloride, action of, with *o*- and *p*-toluidine (REILLY and HICKINBOTTOM), 974.

$C_4H_{11}N$ Diethylamine, preparation of (WERNER), 899; stannochloride of (DRUCE), 715.

4 III

$C_4H_{10}O_2N_2$ Acetiminohydrin, preparation of (RULE), 11.

C_5 Group.

$C_5H_{10}O_3N_4$ Dimethylolcarbamide, preparation of (DIXON), 247.

$C_5H_{11}O_2N$ Methoxyacetiminoethyl ether (RULE), 9.

C_6 Group.

C_6H_6 Benzene, association of organic compounds in solution in (INNES), 410.

6 II

C_6H_6O Phenol, freezing points of mixtures of cresols and (DAWSON and MOUNTFORD), 923; estimation of, in mixtures with cresols (DAWSON and MOUNTFORD), 935.

C_6H_7N Aniline, action of carbon tetrachloride with (HARTUNG), 163.

$C_6H_8N_2$ *m*- and *p*-Phenylenediamine, stanni- and stanno-chlorides of (DRUCE), 716.

$C_6H_{10}O_6$ Dimethyl tartrate, association of, in benzene (INNES), 433.

$C_6H_{12}N_2$ Formaldehydepiperylhydrazone (WEINHAGEN), 586.

6 III

$C_6H_2O_6N_4$ 3:5-Dinitrobenz*iso*oxadiazole oxide (GREEN and ROWE), 70.

$C_6H_{14}O_4N_2$ Methoxyacetiminohydrin (RULE), 9.

C_7 Group.

$C_7H_6O_2$ Benzoic acid, calcium salt, hydrates and alcoholates of (STANBRIDGE), 808.

C_7H_8O *o*-, *m*-, and *p*-Cresol, freezing points of mixtures of phenol and (DAWSON and MOUNTFORD), 923; estimation of, in mixtures with phenol (DAWSON and MOUNTFORD), 935.

C_7H_9N Benzylamine, stanni- and stanno-chlorides of (DRUCE), 717.

Methylaniline, stanni- and stanno-chlorides of (DRUCE), 716.

o-Toluidine, stanni- and stanno-chlorides of (DRUCE), 716.

o- and *p*-Toluidine, action of *n*-butyl chloride on (REILLY and HICKINBOTTOM), 974.

$C_7H_{14}O_6$ β-Methylfructoside, preparation and structure of (STEELE), 257.

γ-Methylgalactoside (CUNNINGHAM), 598.

7 III

$C_7H_5O_8N_3$ Trinitroguaiacol, and its pyridine salt (POLLECOFF and ROBINSON), 653.

$C_7H_6O_6N_2$ Dinitroguaiacols (POLLECOFF and ROBINSON), 649.

C_7H_7ON Formanilide, association of, in benzene (INNES), 432.

$C_7H_8O_3S$ Toluene-*o*- and -*p*-sulphonic acids, analysis of mixtures of (MCKIE), 799.

$C_7H_8O_5N_4$ 3:5-Dinitro-2:6-diaminoanisole (POLLECOFF and ROBINSON), 655.

$C_7H_9O_2N$ Phenylaminoacetic acid, sign of the product in conversion of phenylbromoacetic acid into (SENTER and TUCKER), 140.

7 IV

$C_7H_9O_3NS$ Toluene-*o*- and -*p*-sulphonamides, freezing point curves of mixtures of (McKie), 799.

C_8 Group.

$C_8H_6O_4$ Terephthalic acid, menthyl alkyl esters of (Cohen and de Pennington), 57.

$C_8H_8O_2$ Phenylacetic acid, association of, in benzene (Innes), 432.

$C_8H_8O_3$ Methyl salicylate, association of, in benzene (Innes), 431.

$C_8H_{11}N$ *p*-Methylbenzylamine, stannochloride of (Druce), 718.

8 III

$C_8H_5O_6N$ Nitroterephthalic acid, menthyl alkyl esters of (Cohen and de Pennington), 57.

$C_8H_6O_3N_4$ 4-Acetyl-2- and -3-*p*-phenylene-1-diazo-4-imides (Morgan and Cleage), 591.

$C_8H_7O_3Br$ Phenylbromoacetic acid, sign of the product in conversion of, into phenylaminoacetic acid (Senter and Tucker), 140.

$C_8H_7O_5N$ 6-Nitro-2-methoxybenzoic acid (Simonsen), 782.

$C_8H_7O_8N_3$ 3:5:6-Trinitroveratrole (Pollecoff and Robinson), 654.

$C_8H_8O_3N_2$ *p*-Nitromethylformanilide (Morgan and Grist), 690.

$C_8H_8O_6N_2$ 5:6-Dinitroguaiacol methyl ether (Pollecoff and Robinson), 651.

C_8H_9ON Acetanilide, association of, in benzene (Innes), 433.

Acetophenoneoxime, association of, in benzene (Innes), 432.

$C_8H_9O_2N$ Mandeliminohydrin (Mackenzie), 1; (Rule), 12.

$C_8H_9O_2N_3$ Formylmethylaminobenzene-4-diazohydroxide (Morgan and Grist), 692.

$C_8H_9O_2Br$ 3-Bromoveratrole (Simonsen and Rau), 785.

$C_8H_9O_3N$ 6-Nitro-*o*-tolyl methyl ether (Simonsen), 781.

$C_8H_{10}ON_2$ *p*-Aminomethylformanilide (Morgan and Grist), 691.

$C_8H_{10}O_4N_2$ 5-Nitro-4-aminoveratrole (Simonsen and Rau), 27.

8 IV

$C_8H_5ON_3Cl_2$ 4-Acetyldichloro-*p*-phenylene-1-diazo-4-imides (Morgan and Cleage), 594.

$C_8H_8O_2NCl$ *p*-Chloromandelamide, and its salts (Rule), 17.

$C_8H_{10}O_2NBr$ Bromoaminoveratroles (Simonsen and Rau), 786.

C_9 Group.

$C_9H_8O_2$ Cinnamic acid, association of, in benzene (Innes), 431.

$C_9H_{10}O_3$ Ethyl *p*-hydroxybenzoate, association of, in benzene (Innes), 434.

2-Methoxy-*m*-toluic acid, and its silver salt (Simonsen), 779.

9 III

$C_9H_9O_3Br$ α-Bromo-β-phenylpropionic acid, sign of the product in conversion of, into α-amino-β-phenylpropionic acid (Senter, Drew, and Martin), 151.

$C_9H_9O_4N$ 5-Nitro-2- and -6-methoxy-*m*-tolualdehydes (Simonsen), 778.

$C_9H_9O_5N$ 5-Nitro-2- and -6-methoxy-*m*-toluic acids, and their salts (Simonsen), 779.

$C_9H_{10}O_3N_2$ 4-Nitroaceto-*o*-toluidide, trimorphism of (Chattaway), 897.

$C_9H_{10}O_6N_2$ 6-Nitro-5-amino-3:4-dimethoxybenzoic acid (Simonsen and Rau), 26.

$C_9H_{10}O_7N_2$ 4:6-Dinitro-1:2:3-trimethoxybenzene (Pollecoff and Robinson), 656.

$C_9H_{11}O_2N$ α-Amino-β-phenylpropionic acid, sign of the product in conversion of α-bromo-β-phenylpropionic acid into (SENTER, DREW, and MARTIN), 151.

2-Methoxy-*m*-tolualdoxime (SIMONSEN), 777.

$C_9H_{11}O_2N_3$ Acetylmethylaminobenzene-4-diazohydroxide (MORGAN and GRIST), 692.

$C_9H_{11}O_4N$ 5-Amino-3:4-dimethoxybenzoic acid, and its salts (SIMONSEN and RAU), 24.

$C_9H_{12}ON_2$ *p*-Aminomethylacetanilide (MORGAN and GRIST), 691.

$C_9H_{15}O_3N_3$ Nitrosotriacetonamine, velocity of catalysis of (MCBAIN and BOLAM), 825.

9 IV

$C_9H_{10}O_4NBr$ Bromoaminoveratric acids (SIMONSEN and RAU), 789.

C_{10} Group.

$C_{10}H_{18}$ Hydrocarbon, from spinacene and sodium (CHAPMAN), 464.

10 II

$C_{10}H_8O_2$ 1-Hydrindone-2-carboxylic acid (ROBINSON and CRABTREE), 879.

$C_{10}H_8S_2$ β-Naphthylthiosulphoxylic acid, and its sodium salt (WHITE), 608.

$C_{10}H_9N$ β-Naphthylamine, sulphonation of (GREEN and VAKIL), 35.

$C_{10}H_{10}O_4$ Phenylsuccinic acids, optical activity of, and their esters (WREN), 210.

$C_{10}H_{11}Cl$ α-Chloro-*ar*-tetrahydronaphthalene (GREEN and ROWE), 971.

$C_{10}H_{12}O_4$ 5:6-Dimethoxy-*o*-toluic acid (PERKIN), 762.

$C_{10}H_{13}N$ *ar*-Tetrahydro-α-naphthylamine, preparation and reactions of (GREEN and ROWE), 955.

$C_{10}H_{15}N$ Aminobutylbenzene (REILLY and HICKINBOTTOM), 983.

10 III

$C_{10}H_4O_5N_4$ Dinitronaphth*iso*oxadiazole (GREEN and ROWE), 72.

$C_{10}H_5O_3N_3$ Nitronaphth*iso*oxadiazole (GREEN and ROWE), 72.

$C_{10}H_7ONa$ Sodium α-naphthoxide, relative activity of alkyl iodides with, in methyl alcohol (COX), 821.

Sodium α- and β-naphthoxides, relative activities of alkyl iodides with (COX), 666.

$C_{10}H_{10}O_5N_2$ 2:4-Dinitro-*ar*-tetrahydro-α-naphthol (GREEN and ROWE), 969.

$C_{10}H_{11}O_3N$ 2- and 4-Nitro-*ar*-tetrahydro-α-naphthol (GREEN and ROWE), 968.

$C_{10}H_{11}O_4N_3$ 2:4-Dinitro-*ar*-tetrahydro-α-naphthylamine, and its potassium salt (GREEN and ROWE), 962.

$C_{10}H_{12}O_3N_2$ 4-Nitro-*ar*-tetrahydro-α-naphthylamine, and its salts (GREEN and ROWE), 960.

$C_{10}H_{12}O_4N_4$ Semicarbazones of 5-nitro-2- and -6-methoxy-*m*-tolualdehydes (SIMONSEN), 778.

$C_{10}H_{14}O_4S$ *ar*-Tetrahydro-α-naphthol-4-sulphonic acid, and its sodium salt (GREEN and ROWE), 967.

$C_{10}H_{12}O_5N_2$ 5-Nitro-4-acetylaminoveratrole (SIMONSEN and RAU), 27.

$C_{10}H_{13}O_2N_3$ 2-Methoxy-*m*-tolualdehyde semicarbazone (SIMONSEN), 777.

$C_{10}H_{17}ON$ Camphoroxime, association of, in benzene (INNES), 432.

10 IV

$C_{10}H_9O_4N_2Cl$ 1-Chloro-2:4-dinitro-*ar*-tetrahydronaphthalene (GREEN and ROWE), 972.

$C_{10}H_{11}O_6NS$ 2-Nitro-*ar*-tetrahydro-α-naphthol-4-sulphonic acid (GREEN and ROWE), 967.

$C_{10}H_{12}O_2NCl$ *p*-Chloromandeliminohydrin (RULE), 15.

$C_{10}H_{12}O_3NBr$ Bromoacetylaminoveratroles (SIMONSEN and RAU), 785, 790.

C_{11} Group.

$C_{11}H_{17}N$ *n*-Butyl-*o*- and -*p*-toluidines, and their salts (REILLY and HICKINBOTTOM), 978.

$C_{11}H_{22}O_6$ Tetramethyl-γ-methylgalactoside (CUNNINGHAM), 599.

Tetramethyl-β-methylglucoside, preparation of (HAWORTH and LEITCH), 194.

11 III

$C_{11}H_{12}O_7N_2$ 6-Nitro-5-acetylamino-3:4-dimethoxybenzoic acid (SIMONSEN and RAU), 25.

$C_{11}H_{13}O_4Br$ 6-Bromo-3:4-dimethoxy-β-phenylpropionic acid (CRABTREE and ROBINSON), 871.

$C_{11}H_{13}O_5N$ Acetylamino-3:4-dimethoxybenzoic acids (SIMONSEN and RAU), 25.

$C_{11}H_{13}O_7N_5$ 2:3:5-Trinitro *p*-tolyl-*n*-butylnitrosoamine (REILLY and HICKINBOTTOM), 993.

$C_{11}H_{13}O_8N_5$ 2:3:5-Trinitro-*p*-tolyl-*n*-butylnitroamine (REILLY and HICKINBOTTOM), 993.

$C_{11}H_{14}O_5N_4$ 3:5-Dinitro-*p*-tolyl-*n*-butylnitrosoamine (REILLY and HICKINBOTTOM), 991.

$C_{11}H_{14}O_6N_4$ 3:5-Dinitro-*p*-tolyl-*n*-butylnitroamine (REILLY and HICKINBOTTOM), 992.

$C_{11}H_{13}O_3N_3$ 2-Nitro-*p*-tolyl-*n*-butylnitrosoamine (REILLY and HICKINBOTTOM), 989.

$C_{11}H_{13}O_4N_3$ 3:5-Dinitro-*n*-butyl-*p*-toluidine (REILLY and HICKINBOTTOM), 990.

$C_{11}H_{16}ON_2$ 5-Nitroso-*n*-butyl-*o*-toluidine, and its salts (REILLY and HICKINBOTTOM), 982.

o- and *p*-Tolyl-*n*-butylnitrosoamine (REILLY and HICKINBOTTOM), 979.

$C_{11}H_{16}O_2N_2$ Nitro-*n*-butyl-*p*-toluidines, and their salts (REILLY and HICKINBOTTOM), 988.

11 IV

$C_{11}H_{12}O_6NBr$ Bromoacetylaminoveratric acids (SIMONSEN and RAU), 788.

C_{12} Group.

$C_{12}H_{10}N_2$ Azobenzene, association of, in benzene and alcohol (INNES), 430.

$C_{12}H_{22}O_{11}$ Lactose and Melibiose, constitution of (HAWORTH and LEITCH), 188.

12 III

$C_{12}H_4O_6N_4$ Dinitronaphth*iso*xadiazole oxide (GREEN and ROWE), 71.

$C_{12}H_{12}O_5N_2$ 2:4-Dinitro-*ar*-tetrahydroaceto-α-naphthalide (GREEN and ROWE), 961.

$C_{12}H_{14}O_3N_2$ 4-Nitro-*ar*-tetrahydroaceto-α-naphthalide (GREEN and ROWE), 959.

$C_{12}H_{15}O_4N$ Cotarnine, sodium salt (RAKSHIT), 469.

$C_{12}H_{16}ON_2$ 1-Acetyl-*ar*-tetrahydro-1:4-naphthylenediamine (GREEN and ROWE), 959.

p-Hydroxybenzaldehydepiperylhydrazone (WEINHAGEN), 586.

Salicylaldehydepiperylhydrazone (WEINHAGEN), 585.

C_{13} Group.

$C_{13}H_{10}O$ Benzophenone, association of, in benzene (INNES), 430.
$C_{13}H_{19}N_3$ *p*-Aminoacetophenonepiperylhydrazone (+H_2O) (WEINHAGEN), 587.
$C_{13}H_{24}O_{11}$ Methyldigalactoside (CUNNINGHAM), 602.

13 III

$C_{13}H_{11}ON$ Formyldiphenylamine, association of, in benzene (INNES), 431.
$C_{13}H_{11}O_2N$ 2:4-Dihydroxybenzylideneaniline (SENIER and GALLAGHER), 33.
$C_{13}H_{14}O_2N_2$ Piperonalpiperylhydrazone (WEINHAGEN), 585.
$C_{13}H_{17}O_5N_3$ 3:5-Dinitroaceto-*n*-butyl-*p*-toluidide (REILLY and HICKINBOTTOM), 990.
$C_{13}H_{15}ON_3$ Anisaldehydepiperylhydrazone (WEINHAGEN), 586.
$C_{13}H_{18}O_3N_2$ Nitroaceto-*n*-butyl-*p*-toluidides (REILLY and HICKINBOTTOM), 989.
$C_{13}H_{19}ON$ Aceto-*n*-butyl-*o*- and -*p*-toluidides (REILLY and HICKINBOTTOM), 979.

13 IV

$C_{13}H_{10}O_2NBr$ 2:4-Dihydroxybenzylidenebromoanilines (SENIER and GALLAGHER), 34.

C_{14} Group.

$C_{14}H_{10}$ Phenanthrene, association of, in benzene and alcohol (INNES), 431.

14 II

$C_{14}H_8O_2$ 3:4-Phenanthraquinone (BARGER), 220.
$C_{14}H_{10}O_2$ Benzil, association of, in benzene and alcohol (INNES), 430.
3:4-Dihydroxyphenanthrene (*morphol*), synthesis of (BARGER), 218.
$C_{14}H_{23}N$ Di-*n*-butylaniline, and its salts (REILLY and HICKINBOTTOM), 99.
$C_{14}H_{24}N_2$ *p*-Phenylenedi-*n*-butyldiamine, and its hydrochloride (REILLY and HICKINBOTTOM), 107.

14 III

$C_{14}H_{11}O_2N$ γ-Benzilmonoxime, association of, in benzene (INNES), 432.
$C_{14}H_{13}O_2N$ 2:4-Dihydroxybenzylidene-*m*-toluidine (SENIER and GALLAGHER), 34.
$C_{14}H_{22}ON_2$ *p*-Nitrosodi-*n*-butylaniline, and its salts (REILLY and HICKINBOTTOM), 103.

C_{15} Group.

$C_{15}H_{10}O_5$ Morindone, constitution and reactions of (SIMONSEN), 766.
$C_{15}H_{10}O_6$ Santol (O'NEILL and PERKIN), 137.
$C_{15}H_{25}N$ Di-*n*-butyl-*p*-toluidine, and its salts (REILLY and HICKINBOTTOM), 980.

15 III

$C_{15}H_{10}O_{13}N_4$ 3:5-Dinitro-2-methoxyphenyl carbonate (POLLECOFF and ROBINSON), 649.
$C_{15}H_{12}O_9N_2$ 5-Nitro-2-methoxyphenyl carbonate (POLLECOFF and ROBINSON), 648.
$C_{15}H_{12}NCl$ Cinnamylidenechloroanilines (SENIER and GALLAGHER), 30.
$C_{15}H_{12}NBr$ Cinnamylidenebromoanilines (SENIER and GALLAGHER), 30.
$C_{15}H_{24}O_2N_2$ 2-Nitrodi-*n*-butyl-*p*-toluidine, and its hydrochloride (REILLY and HICKINBOTTOM), 994.

15 IV

$C_{15}H_{14}O_3NBr$ Benzoyl derivatives of bromoaminoveratroles (SIMONSEN and RAU), 786.

C_{16} Group.

$C_{16}H_{10}O_3$ 7-Hydroxy-4:3-indeno-1:2-benzoquinone (ROBINSON and CRABTREE), 879.

$C_{16}H_{12}O_3$ *r*-Diphenylsuccinic anhydride, action of alcohols and amines on (WREN and WILLIAMS), 832.

7-Methoxyphenylbenzopyrones (ROBINSON and TURNER), 875.

$C_{16}H_{12}O_5$ *iso*Brazilein, synthesis of salts of (CRABTREE and ROBINSON), 859.

Morindone methyl ether (SIMONSEN), 773.

$C_{16}H_{12}O_6$ Santal (O'NEILL and PERKIN), 136.

$C_{16}H_{14}O_4$ Diphenylsuccinic acids, optical activity of, and their esters (WREN), 210.

$C_{16}H_{16}O_3$ 2-Hydroxy-4-methoxyphenyl phenylethyl ketone (CRABTREE and ROBINSON), 870.

$C_{16}H_{32}O_2$ Palmitic acid, cerous salt (MORRELL), 116.

$C_{16}H_{34}O$ Hexadecyl alcohol, association of, in benzene and alcohol (INNES), 431.

16 III

$C_{16}H_{13}O_2Cl$ 7-Methoxy-2-phenyl-1:4-benzopyranol anhydrohydrochloride ($+3H_2O$), (ROBINSON and TURNER), 877.

$C_{16}H_{14}O_2N_2$ Cinnamylidenenitrotoluidines (SENIER and GALLAGHER), 31.

$C_{16}H_{15}ON$ Cinnamylidene-*p*-anisidine (SENIER and GALLAGHER), 31.

$C_{16}H_{18}O_4N_2$ 2:4-Dinitro-*ac*- and -*ar*-tetrahydro-α-naphthylamines (GREEN and ROWE), 972.

$C_{16}H_{18}O_2N_2$ Phenylacetiminohydrin (RULE), 11.

$C_{16}H_{18}O_4N_2$ Mandeliminohydrin, preparation of (RULE), 12.

16 IV

$C_{16}H_{19}O_3N_3S$ 4-*p*-Sulphobenzeneazo-*n*-butylaniline, sodium salt (REILLY and HICKINBOTTOM), 111.

C_{17} Group.

$C_{17}H_{14}O_3$ 3-Acetyl-2-phenyl-1:4-benzopyranol or 3-Benzoyl-2-methyl-1:4-benzopyranol ($+H_2O$), and its anhydrohydrochloride (CHATTERJI and GHOSH), 446.

7-Hydroxy-3-benzyl-2-methyl-1:4-benzopyrone (CRABTREE and ROBINSON), 867.

Salicylidenebenzoylacetone ($+\frac{1}{2}H_2O$), and its anhydrohydrochloride (CHATTERJI and GHOSH), 447.

$C_{17}H_{16}O_3$ Substance, from acetylacetone and salicylaldehyde (CHATTERJI and GHOSH), 448.

$C_{17}H_{16}O_4$ 2:4-Dimethoxydibenzoylmethane (ROBINSON and TURNER), 876.

Methyl hydrogen *r*-diphenylsuccinate, and its sodium salt (WREN and WILLIAMS), 837.

$C_{17}H_{17}N$ Cinnamylidene-*p*-xylidine (SENIER and GALLAGHER), 32.

17 III

$C_{17}H_{13}O_2N$ 2:4-Dihydroxybenzylidene-β-naphthylamine (SENIER and GALLAGHER), 34.

$C_{17}H_{17}ON$ Cinnamylidene-*p*-phenetidine (SENIER and GALLAGHER), 32.

$C_{17}H_{19}O_3N$ Morphine, calcium salt (RAKSHIT), 470.

$C_{17}H_{20}O_3N_4$ Osazone of sugar from morindin (SIMONSEN), 774.

$C_{17}H_{23}O_2N$ 2:4-Dihydroxybenzylidenecamphylamine (SENIER and GALLAGHER), 35.

17 IV

$C_{17}H_{21}O_3N_3S$ 4-Methyl-*N*-*n*-butyldiazoaminobenzene-4′-sulphonic acid, and its salts (REILLY and HICKINBOTTOM), 984.

C_{18} Group.

$C_{18}H_{16}O_3$ 7-Hydroxy-3-benzyl-2-methyl-1:4-benzopyrone methyl ether (Crabtree and Robinson), 867.

$C_{18}H_{16}O_5$ Morindone trimethyl ether (Simonsen), 772.

$C_{18}H_{18}O_4$ Ethyl hydrogen *r*- and *meso*-diphenylsuccinates, and their metallic salts (Wren and Williams), 835.

$C_{18}H_{20}O_5$ 2-Hydroxy-4-methoxyphenyl 3:4-dimethoxyphenylethyl ketone (Crabtree and Robinson), 871.

$C_{18}H_{24}O_4$ Menthyl hydrogen terephthalate (Cohen and de Pennington), 64.

$C_{18}H_{30}O_2$ Linolenic acid, cerous salt (Morrell), 119.

$C_{18}H_{32}O_2$ α- and β-Elaeostearic acids, cerous and lead salts (Morrell), 117.
Linoleic acid, cerous salt (Morrell), 117.

$C_{18}H_{34}O_2$ Elaidic acid, cerous salt (Morrell), 117.
Oleic acid, and its potassium salt, molecular condition of, in alcoholic solution (Laing), 435; cerous salt (Morrell), 117.

$C_{18}H_{36}O_2$ Stearic acid, cerous salt (Morrell), 112.

18 III

$C_{18}H_{15}O_3N_3$ Formylmethylaminobenzene-4-azo-β-naphthol (Morgan and Grist), 692.

$C_{18}H_{18}O_2N_2$ Cinnamylidenenitro-ψ-cumidine (Senier and Gallagher), 32.

$C_{18}H_{19}O_4N$ α-Imino-ββ-diphenyldipropionic acid (Senter, Drew, and Martin), 161.

$C_{18}H_{21}ON$ Benzo-*n*-butyl-*p*-toluidide (Reilly and Hickinbottom), 979.

$C_{18}H_{21}O_3N$ Codeine, potassium and sodium salts of (Rakshit), 466.

$C_{18}H_{23}O_4N$ Menthyl hydrogen nitroterephthalate (Cohen and de Pennington), 64.

C_{19} Group.

$C_{19}H_{16}O_4$ 7-Acetoxy-3-benzyl-2-methyl-1:4-benzopyrone (Crabtree and Robinson), 867.

$C_{19}H_{26}O_4$ Methyl menthyl terephthalate (Cohen and de Pennington), 63.

$C_{19}H_{36}O_{11}$ Hexamethyl methyllactoside (Haworth and Leitch), 195.

19 III

$C_{19}H_{25}O_6N$ *o*-Nitromethyl menthyl terephthalate (Cohen and de Pennington), 66.

C_{20} Group.

$C_{20}H_{14}O_4$ 3′:4′-Methylenedioxy-2-phenyl-2:3-dihydro-1:4-α-naphthapyrone (Crabtree and Robinson), 865.

$C_{20}H_{14}O_7$ Diacetylmorindone methyl ether (Simonsen), 774.

$C_{20}H_{20}O_4$ Berberidene (Perkin), 761.

$C_{20}H_{20}O_5$ Ketodihydroberberidene (Perkin), 763.

$C_{20}H_{28}O_4$ Ethyl menthyl terephthalate (Cohen and de Pennington), 63.

$C_{20}H_{30}O_2$ Abietic acid, cerous salt (Morrell), 120.

$C_{20}H_{38}O_{11}$ Heptamethyl methyllactoside (Haworth and Leitch), 195.
Octamethyl digalactose (Cunningham), 601.

20 III

$C_{20}H_{13}O_2N$ *N*-Phenoxyacetylcarbazole (Copisarow), 818.

$C_{20}H_{17}O_2N_3$ Acetylmethylaminobenzene-4-azo-β-naphthol (Morgan and Grist), 694.

$C_{20}H_{17}O_5N$ Oxyberberine, preparation of (Perkin), 737.
n- and *iso*-Oxy*epi*berberines (Perkin), 518.

$C_{20}H_{19}O_4N$ Dihydroanhydro-*n*- and -*epi*-berberines, and their salts (PERKIN), 506, 737.
$C_{20}H_{19}O_5N$ *epi*Berberine, and its salts (PERKIN), 492.
$C_{20}H_{21}O_4N$ Tetrahydroanhydro*epi*berberine, and its salts PERKIN), 510.
$C_{20}H_{27}O_6N$ Nitroethyl menthyl terephthalates (COHEN and DE PENNINGTON), 66.

20 IV

$C_{20}H_{27}O_3N_2S$ 4-*p*-Sulphobenzeneazodi-*n*-butylaniline, sodium and potassium salts (REILLY and HICKINBOTTOM), 109.

C_{21} Group.

$C_{21}H_{16}O_6$ Acetylmorindone (SIMONSEN), 770.

21 III

$C_{21}H_{14}O_3N_2$ Hydroxymethoxyphenanthraphenazines (POLLECOFF and ROBINSON), 651.
$C_{21}H_{20}O_7N_2$ 5:5′-Dinitro-2:2′- and -4:4′-dimethoxydi-3-*m*-methylstyryl ketones (SIMONSEN), 778.
$C_{21}H_{21}O_4N$ Anhydromethylberberines, and their salts (PERKIN), 746, 756.
$C_{21}H_{21}O_5N$ *O*-Methyl*epi*berberine (PERKIN), 520.
$C_{21}H_{21}O_7N$ Trioxyanhydromethylberberine (PERKIN), 747.
$C_{21}H_{23}O_5N$ Hydroxy*iso*anhydrodihydromethylberberines (PERKIN), 752.
$C_{21}H_{23}O_5N_3$ Semicarbazone of ketodihydroberberidene (PERKIN), 763.
$C_{21}H_{25}ON$ *N*-*n*-Nonoylcarbazole (COPISAROW), 818.
$C_{21}H_{25}O_4N$ Dihydromethyl*iso*tetrahydroanhydroberberine, and its salts (PERKIN), 759.

21 IV

$C_{21}H_{22}O_4NCl$ ψ-Methylberberinium chloride (+H_2O) (PERKIN), 750.
$C_{21}H_{22}O_4NI$ ψ-Berberinium iodide (PERKIN), 751.
$C_{21}H_{24}O_4NI$ *N*-Methyl*iso*tetrahydroanhydroberberine hydriodide (PERKIN), 748.

C_{22} Group.

$C_{22}H_{18}O_3$ 7-Methoxy-2:4-diphenyl-1:4-benzopyranol, and its salts (ROBINSON and TURNER), 877.

22 III

$C_{22}H_{19}O_3N$ *r*-Diphenylsuccinanilic acid (WREN and WILLIAMS), 837.
$C_{22}H_{23}O_5N$ *O*-Ethyl*epi*berberine (PERKIN), 521.
$C_{22}H_{23}O_7N$ Narcotine, potassium and sodium salts (RAKSHIT), 467.
$C_{22}H_{27}O_4N$ Dihydrodimethyl*iso*tetrahydroanhydroberberine, and its salts (PERKIN), 760.
$C_{22}H_{31}O_6N$ Nitrobutyl menthyl terephthalates (COHEN and DE PENNINGTON), 66.

C_{23} Group.

$C_{23}H_{19}O_2N$ Diphenylsuccino-*p*-tolil (WREN and WILLIAMS), 839.
$C_{23}H_{21}O_3N$ *meso*- and *r*-Diphenylsuccino-*p*-toluidic acid, and the silver salt of the latter (WREN and WILLIAMS), 838.
$C_{23}H_{22}O_2N_2$ Phenylhydrazone of substance $C_{17}H_{16}O_3$ (CHATTERJI and GHOSH), 449.
$C_{23}H_{29}O_5N$ Anhydro*epi*berberineacetone (PERKIN), 521.
$C_{23}H_{25}O_6N$ Acetoxy*iso*anhydrodihydromethylberberines (PERKIN), 754.

C_{24} Group.

$C_{24}H_{20}N_2$ Dicinnamylidene-*p*-phenylenediamine (SENIER and GALLAGHER), 32.

$C_{24}H_{22}O_5$ Substance, from acetylacetone and salicylaldehyde (CHATTERJI and GHOSH), 449.
$C_{24}H_{24}O_7$ Deoxy-*n*- and -*iso*-santalin (O'NEILL and PERKIN), 130, 133.
$C_{24}H_{24}O_8$ *n*- and *iso*-Santalin (O'NEILL and PERKIN), 127, 131.
$C_{24}H_{34}O_4$ *cyclo*Hexyl menthyl terephthalate (COHEN and DE PENNINGTON), 63.

24 III

$C_{24}H_{23}O_3N$ Methyl *r*-diphenylsuccino-*p*-toluidate (WREN and WILLIAMS), 839.
$C_{24}H_{29}ON_3$ 4-Di-*n*-butylaminobenzeneazo-β-naphthol (REILLY and HICKINBOTTOM), 108.

C_{25} Group.

$C_{25}H_{24}O_7$ Santalone (O'NEILL and PERKIN), 138.
$C_{25}H_{44}O_{21}$ Methyltetragalactoside and Methyltetraglucoside (CUNNINGHAM), 606.

25 III

$C_{25}H_{16}ON_2$ *N*-Carbonylcarbazole (COPISAROW), 819.

C_{26} Group.

$C_{26}H_{22}N_2$ Dicinnamylidene-*o*-naphthylenediamine (SENIER and GALLAGHER), 33.
$C_{26}H_{40}O_4$ Octyl menthyl terephthalate (COHEN and DE PENNINGTON), 63.

26 III

$C_{26}H_{16}O_2N_2$ *N*-Oxalylcarbazole (COPISAROW), 819.

C_{27} Group.

$C_{27}H_{26}O_3$ Substance ($+\frac{1}{2}H_2O$), from benzoylacetone and salicylaldehyde (CHATTERJI and GHOSH), 446.

C_{28} Group.

$C_{28}H_{16}O_4$ α-Naphtholphthalein, preparation of (WERNER), 20.
$C_{28}H_{18}O_6$ Piperonylidene derivative of 3′:4′-methylenedioxy-2-phenyl-2:3-dihydro-1:4-α-naphthapyrone (CRABTREE and ROBINSON), 865.
$C_{28}H_{21}N$ Tetraphenylpyrrole, synthesis of (G. M. and R. ROBINSON), 639.
$C_{28}H_{42}O_4$ Menthyl terephthalate (COHEN and DE PENNINGTON), 64.

28 III

$C_{28}H_{39}ON$ *N*-Palmitylcarbazole (COPISAROW), 819.
$C_{28}H_{41}O_6N$ Menthyl nitroterephthalate (COHEN and DE PENNINGTON), 64.

C_{29} Group.

$C_{29}H_{48}$ Spinacene, analysis and reactions of, and its hexahydro-bromide and -chloride (CHAPMAN), 458.

29 III

$C_{29}H_{40}O_4N_2$ *iso*Emetine ($+H_2O$), and its salts (PYMAN), 226.

C_{30} Group.

$C_{30}H_{24}N_2$ Dicinnamylidenebenzidine (SENIER and GALLAGHER), 33.

30 III

$C_{30}H_{42}O_4N_2$ *N*-Methyl*iso*emetine (PYMAN), 228.

C_{32} Group.

$C_{32}H_{30}O_{12}$ Acetyl-*n*- and -*iso*-santalin (O'NEILL and PERKIN), 128.
$C_{32}H_{32}O_{11}$ Acetyldeoxy-*n*- and -*iso*-santalin (O'NEILL and PERKIN), 130, 134.

32 III

$C_{32}H_{46}O_4N_2$ *N*-Methyl*iso*emetinemethine, and its salts (PYMAN), 229.

32 IV

$C_{32}H_{48}O_4N_2Cl_2$ *N*-Methylemetine methochlorides (PYMAN), 233.
$C_{32}H_{48}O_4N_2I_2$ *N*-Methyl-*n*- and -*iso*-emetine methiodides (PYMAN), 233.

C_{35} Group.

$C_{35}H_{39}O_5N_5$ Ergotinine, supposed formation of ergotoxine ethyl ester from (BARGER and EWINS), 235.
$C_{33}H_{41}O_6N_5$ Ergotoxine, formation of the phosphate of, from ergotinine (BARGER and EWINS), 235.

C_{36} Group.

$C_{24}H_{22}O_8$ Benzoylmorindone (SIMONSEN), 771.

C_{37} Group.

$C_{37}H_{64}O_{31}$ Methyltrimaltoside ($+ H_2O$) (CUNNINGHAM), 607

ERRATA.

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Page	Line	
243	15*	*for* "water" *read* "oxygen."
774	15*	,, "sodium hypochlorite" *read* "potassium permanganate."

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31	19	,,	"$C_{16}H_{15}O_3N_2$" *read* "$C_{16}H_{14}O_3N_2$."
100	3*	,,	"4-*di*-n-*butylaminoazobenzene*-4′-*sulphonic acid*" read "4-p-*sulphobenzeneazodi*-n-*butylaniline*."
100	1	,,	"4-n-*butylaminoazobenzene*-4′-*sulphonic acid*" read "4-p-*sulphobenzeneazo*-n-*butylaniline*."
122	16*	,,	"$Ce_2(C_{18}H_{31}O_2.O)_3$" *read* "$Ce(C_{18}H_{31}O_2.O_2)_3$."
123	4	,,	"(Average temperature)" *read* "(Room temperature)."
540	4	,,	"+ 50·6°" *read* "— 50·6°."
774	6	,,	"$C_{20}H_{15}O_7$" *read* "$C_{20}H_{14}O_7$."

* From bottom.